WAR GASES

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THE WAR GASES

WAR GASES

Their Identification and Decontamination

BY

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PREFACE

Relatively little has been written in the United States of America on the subject of passive defense, or as we would put it, civilian defense against poison gas. One of the very first steps in defense of this nature is a system for the detection, the sampling and the identification of the chemical warfare agents, and the decontamination of areas and materials polluted by them.

It is the aim of this book to present these subjects so that the information given will be useful to the gas identification officer, the war gas chemist, the decontamination officer, and the health officer. While this book was written primarily for the aforementioned officers, Chapters I, II, III, part of IV and VII should prove of value to the air raid warden and, in general, to all persons dealing with the above mentioned phases of gas defense. It is written so that it can be used for the training of gas identification officers, as a manual by chemists and decontamination officers, and as a source of information on the analytical chemistry of the war gases. It should be useful even in the Theater of Operations, not so much for initial detection, for which sensory methods are possibly best, but rather for the delineation of the extent of contamination and estimation of the degree of contamination.

The risk and danger inherent in the use of poison gas compels us to be prepared to meet such a form of attack. Preparation for the detection, identification and decontamination of war gases is a long step forward in the ability to repel successfully such types of attack. It is the hope of the author that this book will be of some help in this preparation.

The author wishes to thank Margaret Jacobs, Roberta Leah Jacobs and Berenice Anita Jacobs for their aid in reading proof and in the preparation of the index.

The author has tried to give adequate acknowledgment for the use of methods, procedures, tables, etc., either in the text, or at the beginning or end of each chapter. If any reference is omitted, such omission is entirely unintentional. The author will be pleased to correct such omissions if brought to his attention.

Brooklyn, N. Y. 1942. M. B. J.

NOTE

The subject matter of this book has been obtained from the most recent literature, particularly with respect to analytical procedures. The opinions expressed are those of the author and it is to be understood that he does not presume to give the official views of any branch of the Federal, State or City Government.

M. B. J.

CONTENTS

Frequently Used Terms

1) The term water used in the methods means distilled water.

2) The terms alcohol and ether refer respectively to 95 per cent ethyl alcohol and to ethyl ether.

3) The following reagents, unless otherwise specified or qualified in the text, have the approximate strength stated and conform in purity with the requirements of the United States Pharmacopoeia.

sulfuric acid	specific gravity 1.84
hydrochloric acid	specific gravity 1.184
nitric acid	specific gravity 1.42
fuming nitric acid	specific gravity 1.50
glacial acetic acid	specific gravity 1.048 (25°C.)
hydrobromic acid	specific gravity 1.38
phosphoric acid	85 per cent strength by weight
ammonium hydroxide	specific gravity 0.90

4) All other reagents and test solutions, unless otherwise described in the text, conform to the specifications of the United States Pharmacopoeia or of the American Chemical Society. When the anhydrous salt is intended to be used, it is so stated; otherwise the salt referred to is the crystallized product.

5) In the expressions (1:2), (5:4), etc., used in connection with the name of a reagent, the first numeral indicates the volume of the reagent used, and the second numeral indicates the volume of water. For example, hydrochloric acid (1:2) means a reagent prepared by mixing one volume of hydrochloric acid with two volumes of water. When one of the reagents is a solid the expression means parts by weight, the first numeral representing the weight of the solid reagent and the second numeral the weight of water in similar units.

6) In making up solutions of definite percentage, it is understood that x grams of substance is dissolved in water or other solvent and made up to 100 ml. Although not theoretically correct, this procedure will not result in any appreciable error in any of the methods given in this book.

7) All calculations are based on the table of international atomic weights.

8) The following abbreviations are used and have the indicated meaning:

ml.	milliliter
l.	liter
C.	Centigrade degrees
F.	Fahrenheit degrees
N	normal, with reference to solutions
mm.	millimeters
mg.	milligrams
mg./l.	milligrams per liter

ppm.	parts per million
mm^3	cubic millimeters
μ	micron
S. T. P.	standard temperature and pressure
lb.	pound
sp. gr.	specific gravity

The abbreviations of periodicals, bulletins, circulars, leaflets, etc., referred to in the footnotes follow the system of *Chemical Abstracts*.

9) In the use of the expression "parts per million of x," it is understood that the expression means parts of x per million parts of air. The author has tried to differentiate when this expression is used with reference to a solution, by the statement "parts of x per million of solution."

I. CLASSIFICATION OF THE CHEMICAL AGENTS

GENERAL REFERENCES

Prentiss, *Chemicals in War*. McGraw-Hill, New York, 1937.
Vedder, *Medical Aspects of Chemical Warfare*. Williams & Wilkins, Baltimore, 1925.
U. S. War Dept., *Technical Manual* 3–215. *Military Chemistry and Chemical Agents*. 1940.
Jacobs, *The Analytical Chemistry of Industrial Poisons, Hazards and Solvents*. Interscience, New York, 1941.

I. Introduction

In the war of today there is little distinction between combatant and non-combatant. The civilian is even more exposed to air attack than the soldier. The Army and Navy have their very important duties to perform. They cannot be expected to regulate and guard civilian life and property in addition to these duties. Indeed, such a step would merely serve to diminish their effective force for operations in the field. For these reasons, it is necessary for the civilian and civilian authorities to play an important role in safeguarding themselves and their community from the attacks of the enemy.

The steady flow of supplies and material to the Army and Navy is the obligation of the civilian. This is, of course, dependent on the energy and morale of the civilian. It is one of the aims of the enemy to break that morale, diminish that energy, and create havoc and panic in the community by air and gas attack. The objects of gas attacks on civilians are

1) To produce casualties by means of the gas itself and thus hospitalize many people,
2) To produce casualties by contaminating streets etc.,
3) To arrest and diminish industrial and commercial activities,
4) To make food and similar stores unfit for use,
5) To cause widespread discomfort, anxiety, disablement, fear, thus lowering the morale of the population and inducing a will to compromise or surrender.

Information as to what the civilian should do in the case of air attack with high explosive has been widespread but similar information concerning poison gas attacks has not been so well disseminated. The Geneva General Gas Protocol of 1925, which most of the countries of Europe signed, forbids the use of poison gas in war. The British Government obtained an undertaking from the enemy not to use poison gas. However, the risk of the use of poison gas remains a strong possibility and therefore cannot be disregarded.

It has been said by some that since war gases have not been used to any great extent as yet in World War II, they will, therefore, not be used. Others claim that it has been proved that the damage resulting from gas attacks by air are not commensurate with the effort; therefore, war gases will not be used. Such complacency is dangerous and is to be deplored. The most plausible reason that war gases have not been used is that European peoples have been prepared for years against such attacks, so that small damage would result; it is unwarranted to believe that gases would not take a heavy toll of a populace which is unprotected and uneducated, insofar as war gases are concerned. Such attacks, launched against an unprepared people, might be extremely serious. We have learned to our sorrow that we must always be on the alert, for our enemies are resourceful and unscrupulous.

Mayor Fiorello H. LaGuardia, U. S. Director Civilian Defense, stated in a foreword to the pamphlet, *Protection Against Gas*, "If war gas were to be used in an attack upon this country, an enemy probably would act without warning in order to exploit the effect to the utmost. Thorough preparation is the surest way to reduce the number of casualties and perhaps even to discourage the use of war gas entirely."

Poison gas is a formidable weapon but there is no mystery in its use and little in its action. It is possible that an entirely new chemical agent may be developed by the enemy but the precautions to be observed against those which were used in World War I and other known chemical agents will aid in the prevention of casualties or damage from any newly developed chemical weapon.

For years before the Second World War, the general public was given an oversupply of nonsense on the dangers of poison gas. Poison gas is dangerous; that is why it is used as a weapon in war. Because it is a menace, we must be careful. It is not so dangerous, however, that we cannot protect ourselves against it. Mustard gas was, and probably is, the most efficient chemical warfare agent known. Yet it took 1 ton of mustard to cause 30 casualties in the World War and only 1 of these casualties was fatal.

Few pamphlets and books on first-aid give directions for the administration of first-aid to gas casualties. The author urges the reader to become acquainted with first-aid treatment of gas casualties and to procure a modern outline of such treatment as is described in the publications of the

Office of Civilian Defense,[1] the U. S. War Dept.,[2,3] and in British publications.[4]

The danger from air attacks on civilian centers in which poison gas is a menace to ourselves and our food supply is less than that from high explosive because the damage wrought by the latter will generally be greater.

In order that we may know how to evaluate the danger from poison gases and the means of protection against them, we must learn about their physical, chemical and physiological properties.

It is a popular belief that new and deadly chemical agents can be made at will but, fortunately, this is a practical misconception because of the rigid requirements of a chemical warfare agent. It has been said that thousands of substances were considered as possible chemical agents. Only about 3,000 were actually investigated to determine their value as poison gases and of these only 38 were actually used in war. It can be added that, of these 38, only 10 or 12 were used to any extent and that, of these 10 or 12, only 6 were really efficient or of great importance as warfare agents.

A search of the literature leads to the conclusion that the following chemical warfare agents are the ones which will most likely be used in gas attacks:

Mustard gas
Lewisite
Ethyldichloroarsine
Phosgene
Diphosgene
Bromobenzyl cyanide
Ethyliodoacetate
Chloroacetophenone
Chloropicrin
Diphenylchloroarsine
Diphenylaminechloroarsine
Phosphorus

Particular stress will therefore be placed on these agents throughout the book. However, for the sake of completeness and because it is well not to overlook the possibility that other chemical agents may be employed, war gases less likely to be used will also be included. Gases like hydrogen

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[1] U. S. Office of Civilian Defense, *Protection Against Gas*. 1940.

[2] U. S. War Dept., *Basic Field Manual* 21–40, *Defense Against Chemical Attack*. 1940.

[3] U. S. War Dept., *Basic Field Manual* 21–40, *Military Sanitation and First Aid*. 1940.

[4] Ministry of Home Security, Brit., *A. R. P. Handbook* No. 1, *Personal Protection Against Gas*. 1939.

sulfide, carbon monoxide, hydrogen cyanide and arsine which are likely to arise as decomposition products of other agents will also be discussed.

II. Definition of Terms

For a resumé of elementary chemistry, physics and meteorology as applied to chemical warfare the reader is referred to Vedder[5] and to the *U. S. Army Technical Manual 3–215, Military Chemistry and Chemical Agents.* The terms *gas, persistent, non-persistent, concentration, decontamination* etc. will be used so often that it will be best to define them adequately.

1. CHEMICAL WARFARE AGENT

The broad definition of a chemical warfare agent is: any chemical substance used in warfare. This substance, after release and, as a direct consequence of its chemical properties, must be able to produce a toxic effect, a powerful irritant effect, a screening smoke, or an incendiary action. It is not limited to the so-called "war gases" but also includes any gaseous, liquid, or solid substance used in warfare. This definition, then, includes the war gases, screening smokes, incendiaries, but not necessarily, explosives.

War Gas.—More particularly, a *war gas* is any chemical substance, whether solid, liquid or gaseous, that produces a physiological response in a human body. Expressed mathematically, a war gas is any substance which, at a concentration of 4 grams per cubic meter in air, creates an atmosphere capable of provoking fatal lesions in the respiratory apparatus of a man or animal remaining in it for 5 minutes. The concentration stated is merely a limiting value, for substances are used which are active and lethal at much lower concentrations.[6]

Toxic Agent.—This is a substance which, as a result of its chemical properties and by its ordinary action, produces a deleterious physiological effect when applied to the body externally, when inhaled, or when taken internally in moderate doses.

Criteria for an Effective Chemical Agent.—A chemical warfare agent must fulfill several requirements to be an effective one.

(1) It must be highly toxic so that the quantity necessary to produce a given effect will be small.

(2) A war gas must have a vapor density greater than that of air so that it will not diffuse too readily.

(3) If the agent is a real gas, it must be easily compressible, otherwise it cannot be readily stored or placed in shells. If the agent is a liquid or solid, it must be capable of being readily, although usually not too readily, vaporized.

(4) It must be capable of being manufactured on a relatively large scale.

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[5] Vedder, *Medical Aspects of Chemical Warfare.* Williams & Wilkins, Baltimore, 1925.

[6] Herlant, *J. pharm. Belg.*, **31**, 820 (1939).

(5) The raw materials from which it is made must be cheap, domestic products and easily available.

(6) The agent must be capable of being handled and transported with safety. If an agent cannot comply with this requirement, it is relatively useless no matter how lethal it may be for it will cause so many casualties among one's own personnel as to be a handicap rather than an aid.

(7) It must be relatively stable in contact with moisture, otherwise it will be too readily decomposed, as dichloromethyl ether is and thus lose value as an agent.

(8) It must have little corrosive action on metals, otherwise it cannot be stored or placed in shells without special precautions.

(9) It must be stable on storage so that it will not decompose on standing or polymerize to form a harmless substance, as in the case of acrolein.

(10) It must be relatively stable to explosion or else form toxic compounds on explosion, like chloropicrin, otherwise it cannot be dispersed effectively by artillery fire.

2. PERSISTENT AND NON-PERSISTENT AGENTS

Chemical warfare agents are generally divided into two groups, namely, persistent and non-persistent agents. A chemical agent is said to be persistent if ten minutes after its release in the open, under conditions favorable to the agent, there is sufficient war gas remaining at the point of release to necessitate protection for persons in its vicinity. If, at the end of ten minutes, there is insufficient agent remaining to make protection necessary, it is deemed to be a non-persistent agent.

Persistency or non-persistency of a war gas depends chiefly on the rapidity of evaporation of the agent. This is a function of the volatility of the agent which in turn is a function of the vapor pressure, temperature and molecular weight of the substance. Slightly volatile agents are persistent, whereas real gases and highly volatile liquids are non-persistent.

Temperature is of great importance in the actual length of time an agent will contaminate an area. Thus Lewisite, which will last for 24 hours in the open or 2 to 3 days in the woods during summer, will persist for a week in winter. Mustard gas will persist for several weeks in the winter.

Among the more important non-persistent agents are phosgene and, according to the temperature and method of dispersal, chloroacetophenone. Among the more important persistent war gases may be mentioned diphosgene, bromobenzyl cyanide, ethyliodoacetate, mustard gas and Lewisite.

3. CASUALTY AND HARASSING AGENTS

Another system of classification is that of separating the chemical agents into groups depending upon their casualty or harassing effects. A *casualty* agent is a chemical warfare agent whose physical and chemical properties are such that a dangerous or toxic concentration can be set up under field conditions. The vesicants, asphyxiants and paralysants belong to this group.

A *harassing* agent is a chemical warfare agent whose physical and chemical properties are such that it compels the use of masks. This in turn inhibits enemy operations, since personnel is less efficient when masked. The lachrymators and nasal irritants are members of this group.

The principal casualty agents are phosgene, Lewisite, and mustard gas. The principal harassing agents are chloroacetophenone, diphenylaminechloroarsine (Adamsite), diphenylchloroarsine (DA) and similar arsenicals. Chloropicrin is used both as a casualty and harassing agent.

4. CONCENTRATION

Concentration is the amount of a given substance in a stated volume or weight of material. With reference to the war gases, a high or strong concentration means that there is a great deal of war gas in the air; a low or weak concentration means that there is little of the agent in the air.

The gas laws, the derivation and application of which may be found in all books on general chemistry, may be used for the calculation of the concentration of gas in air, for the reduction of gases to standard temperature and pressure, and for the corrections to be applied because of the presence of water vapor.

The lowest concentration of a chemical agent which will produce a physiological response, for instance, involuntary weeping, is called the *threshold of action*, or the lower limit of irritation. Some writers mention as an intermediate concentration one which requires masking.

The *threshold concentration*, or the limit of insupportability, of a chemical agent is the lowest concentration which a normal person cannot tolerate for longer than one minute.

The *lethal concentration* of a chemical agent is the concentration which will kill the average unprotected person. The numerical value of the lethal concentration decreases as the time of exposure increases.

The ability of any chemical warfare agent to injure a person or to cause damage to material depends upon two entirely distinct factors. The first is the concentration of the gas in the air and the second is the length of time of exposure to the chemical agent. The injury and damage sustained is proportional to the product of the concentration and the time of exposure. In other words, the damage is greater if the concentration is high and the time of exposure is long.

Gas Concentrations and Conversion Formulas.—There are a number of different systems for expressing the concentrations of substances in air. These are: parts of the contaminant per million parts of air; milligrams of the contaminant per liter of air; ounces of the contaminant per 1,000 cubic feet of air; per cent by volume of the contaminant in air; milligrams of the contaminant per cubic meter of air. This last expression is used mainly for expressing the concentrations of solids in air. All these expressions are interchangeable. Thus,

$$\frac{\%\text{ by vol.}}{10{,}000} = \text{parts per million}$$

For example, 1% = 10,000 ppm.

In order to convert milligrams per liter, or any other weight per unit volume, into a volume per volume ratio such as parts of vapor per million parts of air, use must be made of the gram-molecular volume relationship, namely that the volume occupied by a gram-molecular weight of a gas at standard temperature and pressure, (0° C. and 760 mm. pressure) is equal to 22.4 liters, or 24.45 liters at 25° C. and 760 mm. pressure. Thus:

$$\text{ppm.} = \frac{24450 \times \text{mg.}}{M} \tag{1}$$

where M is the molecular weight of the substance and the other symbols have the meanings previously assigned. Suppose that, in a determination, it is found that 1 mg. per liter of phosgene is present and it is desired to convert this into parts of phosgene per million of air; then, by substitution in the above formula,

$$\text{ppm.} = \frac{24450 \times 1}{99} = 247 \text{ parts per million}$$

Or, suppose that the result had been calculated on the basis of parts per million and it was desired to convert into mg. per liter; then

$$\text{mg.} = \frac{\text{ppm.} \times M}{24450}$$

If one part per million were found, this would be converted by substitution:

$$\frac{1 \times 99}{24450} = 0.00405 \text{ mg. per liter.}$$

For any multiple of 1 part per million or 1 mg. per liter, the result is obtained by simple multiplication. By use of Appendix Table[7] I, which gives the equivalence between milligrams per liter and parts per million, these calculations are greatly simplified.

To convert from mg. per cubic meter into parts per million, use formula (1) but divide the right hand side of the equation by 1000.

The expression: cubic millimeters per cubic meter is also used occasionally; this is equivalent to parts per billion.

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[7] Fieldner, Katz and Kinney, and Henderson, *U. S. Bur. Mines, Tech. Papers* **248** (1921) Gas Masks for Gases Met in Fighting Fires.

In order to obtain the quantity of a contaminant in an atmosphere which has been sampled by passing it through an absorbent, the analysis is made to find out the per cent of the contaminant in the aliquot part of the absorbing solution taken for analysis. From this result, the total quantity of toxic or hazardous material in the entire volume of the absorbing solution is calculated. From this value and the known volume of the air or atmosphere sampled, the amount of contaminant per unit of air or atmosphere can be computed.

Some factors for conversion of some units are the following:

1) mg./l. x 28.32 = mg./cu. ft.
2) mg./l. x 1000 = mg./cu. m.
3) mg./cu. ft. x 35.314 = mg./cu. m.
4) mg./cu. m. x 0.02832 = mg./cu. ft.
5) mg./l. ≈ oz./1000 cu. ft.

5. VOLATILITY[8]

The amount of a substance present as a vapor in a unit volume of air which is saturated with that substance, is called the volatility of the substance. The volatility increases as the temperature increases. Thus we note that the volatility is related to the term absolute humidity as applied to water.

If the volatility is many times larger than the lethal concentration for a 3 minute exposure, the agent is a casualty agent, since this ratio shows that it is possible to set up a killing concentration under field conditions.

The volatility of a chemical agent may be calculated and expressed in milligrams per liter equivalent to ounces per 1,000 cubic feet by the formula:

$$\text{Volatility} = \frac{M \times P \times 16}{T_2}$$

where M = Molecular Weight
P = Vapor pressure at T_2
T_2 = Absolute temperature of the atmosphere.

6. CONTAMINATION AND DECONTAMINATION

The liquid or vapor remaining in appreciable quantity on a material or a person after exposure to a persistent or a non-persistent agent, is termed *contamination*. Contamination arises mainly from the persistent gases and is caused by splashes of the liquid or air-borne spray.

The treatment or method of procedure used to render such contamination harmless, is termed *decontamination*. When the contaminated ground

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[8] U. S. War Dept., *Technical Manual* 3-215 *Military Chemistry and Chemical Agents*. 1940.

or object has been treated in such a manner that danger from direct contact has been eliminated and dangerous vapor can no longer be given off, it is said to be decontaminated. For practical purposes, decontamination must be considered complete when this result has been achieved, even if the contaminating substance has been only buried or sealed.

These topics will be discussed in some measure in subsequent sections.

III. Classification of the Chemical Agents

Poisonous war gases may be classified simply for the layman into two main groups according to their effect on the body. These categories are: first, the *blister* gases and second the *non-blister* gases. The second group may be further subdivided into lung irritants or choking gases, eye irritants or tear gases, and nose irritants or sneezing gases. Roughly the blister and non-blister gases may also be grouped into the persistent and non-persistent classes.

1. MODIFIED PHYSIOLOGICAL CLASSIFICATION

For scientific purposes, chemical agents may be classified according to (1) chemical structure and chemical action, (2) physical state, (3) type of physiological action, (4) degree of physiological action and (5) tactical use. Classification according to a modified United States system is useful. This system is based mainly on type of physiological action. This classification is by no means a rigid one. The classifying of a chemical agent as a lung irritant, for instance, does not mean that it cannot act as a lachrymator. Many of the war gases really belong to several groups but are classed with the one showing their principal physiological action. The physiological effect caused by an individual agent is given in some detail in Chapter II.

A. War Gases

1. Lung irritants or suffocating agents.—These substances act upon the lungs and are generally fatal in low concentrations for short times of exposure. The more important of these agents are:

Phosgene, CG
Diphosgene, trichloromethylchloroformate
Chloromethylchloroformate
Chloropicrin, PS

2. Irritants, which may be subdivided into

a) Lachrymators.—These substances produce tears and obscure the vision. Some have only a temporary effect, while others are toxic. The more important of the simple lachrymators are:

Bromobenzyl cyanide, CA or BBC
Chloroacetophenone, CN

The most important of the toxic lachrymatory agents is:

Bromoacetone

b) Toxic smokes.—These substances are often called *sternutators.* They cause sneezing, coughing and vomiting in very low concentrations. They cause physical debility and are lethal in higher concentrations. The more important of this group are:

Diphenylchloroarsine, DA
Diphenylcyanoarsine, CD or DC
Diphenylaminechloroarsine, DM

c) Labyrinthic gases.—These substances have an effect on the inner ear, hence disturb the sense of equilibrium and cause falling. These substances are also lung irritants. They did not play any significant rôle in the World War, 1914–1918. The most important of this group is:

Dichloromethyl ether.

3. Vesicants.—These substances cause burns on unprotected skin and when inhaled are lung irritants. The most important are:

Dichloroethyl sulfide, mustard gas, HS
Chlorovinyldichloroarsine, Lewisite, M1

4. Systemic poisons or paralysants.—These substances attack the blood and nervous systems. None of these poisons, among which may be mentioned hydrocyanic acid, carbon monoxide, cyanogen chloride, hydrogen sulfide and nitrous vapors, were of any importance as chemical agents in the World War of 1914–1918.

B. Screening Smokes
C. Incendiaries
D. Explosives. (These substances are generally not considered with chemical warfare agents.)

2. PRENTISS CLASSIFICATION

I) Lachrymators
  A) Simple
    1) Ethylbromoacetate
    2) Xylyl bromide
    3) Benzyl bromide
    4) Bromomethylethyl ketone
    5) Ethyliodoacetate*

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* Indicates those agents which were most effective in World War 1914–1918. Prentiss, *Chemicals in War.* McGraw-Hill, New York, 1937.

        6) Benzyl iodide
        7) Bromobenzyl cyanide*
        8) Chloroacetophenone*
    B) Toxic
        9) Chloroacetone
        10) Bromoacetone*
        11) Iodoacetone
        12) Acrolein

II) Lung Injurants
    A) Simple
        1) Chlorine*
        2) Methylchlorosulfonate
        3) Ethylchlorosulfonate
        4) Monochloromethylchloroformate
        5) Dimethyl sulfate
        6) Perchloromethyl mercaptan
        7) Phosgene*
        8) Trichloromethylchloroformate* (Diphosgene)
        9) Chloropicrin*
        10) Phenylcarbylamine chloride
        11) Dichloromethyl ether
        12) Dibromomethyl ether
    B) Toxic
        13) Phenyldichloroarsine
        14) Ethyldichloroarsine*
        15) Phenyldibromoarsine

III) Systemic Toxics
        1) Hydrogen cyanide
        2) Cyanogen bromide
        3) Cyanogen chloride

IV) Vesicants
        1) Dichloroethyl sulfide* (Mustard Gas)
        2) Chlorovinyldichloroarsine (Lewisite)
        3) Methyldichloroarsine
        4) Dibromoethyl sulfide

V) Respiratory Irritants
        1) Diphenylchloroarsine*
        2) Diphenylcyanoarsine*
        3) Ethylcarbazol
        4) Diphenylaminechloroarsine

3. CHEMICAL CLASSIFICATION OF THE WAR GASES

For the analytical point of view and to stress the chemical relationships of the warfare agents, the classification suggested by Hoogeveen[9] is adequate.

		Molecular weight
I Inorganic War Gases		
Chlorine	Cl_2	70.9
Bromine	Br_2	159.8
II Organic War Gases		
1. Carbonyls and thiocarbonyls		
Phosgene	$COCl_2$	99
Thiophosgene	$CSCl_2$	115
2. Halogenated esters including dimethyl sulfate		
Dimethyl sulfate	$SO_2(OCH_3)_2$	126
Methylchlorosulfonate	$ClSO_2OCH_3$	130.5
Ethylchlorosulfonate	$ClSO_2OC_2H_5$	144.5
Ethylchloroacetate	$CH_2ClCOOC_2H_5$	122.5
Ethylbromoacetate	$CH_2BrCOOC_2H_5$	167
Ethyliodoacetate	$CH_2ICOOC_2H_5$	214
Methylchloroformate	$ClCOOCH_3$	94.5
Chloromethylchloroformate	$ClCOOCH_2Cl$	129
Dichloromethylchloroformate	$ClCOOCHCl_2$	163.4
Diphosgene	$ClCOOCCl_3$	198
3. Halogenated ethers and thioethers		
Dichloromethyl ether	$ClCH_2OCH_2Cl$	114.7
Dibromomethyl ether	$BrCH_2OCH_2Br$	204
Dichloroethyl sulfide (mustard gas)	$(ClCH_2CH_2)_2S$	159
Dibromoethyl sulfide	$(BrCH_2CH_2)_2S$	247.8
4. Halogenated ketones		
Chloroacetone	$ClCH_2COCH_3$	92.5
Bromoacetone	$BrCH_2COCH_3$	136.9
Bromomethylethyl ketone	$BrCH_2COC_2H_5$	151
Chloracetophenone	$ClCH_2COC_6H_5$	154.5
5. Halogenated aromatic hydrocarbons		
Benzyl chloride	$C_6H_5CH_2Cl$	126.5
Benzyl bromide	$C_6H_5CH_2Br$	171
Benzyl iodide	$C_6H_5CH_2I$	218
Bromobenzyl cyanide	$C_6H_5CH(Br)CN$	196
Xylyl bromide	$CH_3C_6H_4CH_2Br$	185
Nitrobenzyl chloride	$NO_2C_6H_4CH_2Cl$	171.5
6. Nitro compounds		
Chloropicrin	CCl_3NO_2	164.5
Bromopicrin	CBr_3NO_2	297.7
Tetrachlorodinitroethane	$Cl_2NO_2CCNO_2Cl_2$	399.6
7. Cyanogen compounds		
Hydrogen cyanide	HCN	27

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[9] Hoogeveen, *Chem. Weekblad*, **34**, 35 (1937).

		Molecular weight
Cyanogen chloride	ClCN	61.4
Cyanogen bromide	BrCN	106
Phenylcarbylamine chloride	$C_6H_5N{:}CCl_2$	175
8. Arsenic compounds		
Methyldichloroarsine	CH_3AsCl_2	161
Ethyldichloroarsine	$C_2H_5AsCl_2$	175
Phenyldichloroarsine	$C_6H_5AsCl_2$	223
Diphenylchloroarsine	$(C_6H_5)_2AsCl$	264.5
Diphenylcyanoarsine	$(C_6H_5)_2AsCN$	255
Phenarsazine chloride	$NH(C_6H_4)_2AsCl$	277.5
Lewisite, Chlorovinyldichloroarsine	$ClCH{:}CHAsCl_2$	207.3

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II. THE PHYSICAL CHARACTERISTICS AND PHYSIOLOGICAL RESPONSE OF THE WAR GASES

GENERAL REFERENCES

Vedder, *Medical Aspects of Chemical Warfare.* Williams & Wilkins Co., Baltimore, 1925.

U. S. War Dept., *Technical Manual 3-215. Military Chemistry and Chemical Agents.* 1940.

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A. THE LUNG IRRITANTS

The lung irritants, choking gases, or lung injurants, as they are termed by Prentiss, have their primary physiological action on the respiratory tract. When inhaled, they cause inflammation of the interior portion of the bronchial tubes and lungs. In high concentrations, they immediately irritate the eyes, producing smarting and watering, and the throat, causing violent coughing and sometimes retching. The latter symptom is particularly true of chloropicrin. High concentrations inhaled for only a short time and low concentrations inhaled for a long time may result in death or in serious injury.

1. CHLORINE

Chlorine is more important as an intermediate in the production of other war gases than as a chemical war agent, itself. Historically it occupies an important position, for it was the first gas used on a large scale in war. It was employed by the Germans against the British and some French troops at Ypres on April 22, 1915. It caused an estimated 15,000 casualties, some 5,000 of which were fatal but this was due mainly to the surprise element and the lack of adequate protection.

Chlorine, Cl, is a heavy greenish-yellow gas which has a characteristic choking and pungent odor with an irritating effect on the nose and throat. It boils at −33.6° C.; melts at −102° C.; has a density of 2.5 referred to air; and can be easily liquefied, for its critical temperature is 146° C. Its specific gravity is 1.41. Its vapor pressure at 20° C. is 6.57 atmospheres, at 30° C. is 8.75 atmospheres and at 40° C. is 11.5 atmospheres. As a liquid, it has a high coefficient of expansion and its solubility in water at 20° C. is 215 volumes in 100 volumes.

Chlorine is a strong lung irritant. Inhalation of chlorine elicits respiratory reflexes and causes coughing, smarting of the eyes, a general feeling of discomfort in the chest, a hoarse cough, nausea, and vomiting. The face may become red and bloated because of venous congestion, or gray in color showing failing circulation. Inhalation of chlorine affects both the lower and upper respiratory tract and produces inflammation of the entire respiratory tract and edema of the lung after severe exposure.[1] The most pronounced symptoms[2] are suffocation, constriction in the chest and tightness in the throat.

Concentrations of 0.1 per cent are lethal for most animals in a few minutes. Exposure to a concentration range of 0.004–0.006 per cent for 30–60 minutes will have fatal or serious consequences. The maximum concentration to which animals can be exposed for a period of 60 minutes without serious disturbances is 0.0004 per cent and the maximum concentration to which they may be exposed for several hours without serious disturbance or with but slight symptoms is 0.0001 per cent by volume.

The least detectable odor of chlorine is 3.5 parts per million.[3] This is small enough to give adequate warning without harmful effect if one can get out of the vicinity immediately.

2. HYDROCHLORIC ACID

The principal hazardous effects of hydrochloric acid, commercial muriatic acid are burns and dermatitis, though its importance as a respiratory irritant should not be overlooked. Hydrogen chloride, HCl, the gas from which the acid is formed, is a colorless, pungent and poisonous substance, which is very soluble in water. It fumes very strongly in air and is extremely corrosive, for the fume is actually composed of minute droplets of hydrochloric acid. This substance is not used itself in war but is the hydrolytic product of many of the war gases and is the basis of the screening smokes derived from such chemical warfare agents as the tin, titanium and silicon tetrachlorides.

Hydrogen chloride gas attacks the upper respiratory tract. The acid formed neutralizes the alkali of the tissues and causes death due to edema or spasm of the larynx and inflammation of the upper respiratory system. Concentrations of 0.13 to 0.2 per cent are lethal for human beings in exposures lasting a few minutes.[4,5,6] Concentrations in the range of 0.1

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[1] Haggard, *J. Ind. Hyg.*, **5**, 397 (1923–4).

[2] Berghoff, *Arch. Internal. Med.*, **24**, 678 (1919).

[3] Sayers, DallaValle and Yant, *Ind. Eng. Chem.*, **26**, 1251 (1934).

[4] Lehmann and Hess as quoted by Flury and Zernik, *Schaedliche Gase*. Springer, Berlin, 1931.

[5] Henderson and Haggard, *Noxious Gases*. Reinhold, New York, 1927.

[6] Sayers, DallaValle and Yant, *Ind. Eng. Chem.*, **26**, 1251 (1934).

to 0.13 per cent are dangerous if breathed for 30 to 60 minutes. The maximum concentration which can be tolerated for exposures of 60 minutes is in the range 0.005 to 0.01 per cent and the maximum tolerated for several hours of exposure is 0.001 to 0.005 per cent.

3. BROMINE

Bromine will probably not be used as a war gas. However, it may occur as an impurity in bromine-containing war gases or as a decomposition product of such gases.

Bromine, Br, is a dark red, almost black, heavy liquid. Its vapor is also dark red in color. It boils at 58.7° C. but vaporizes readily at room temperature. It has a specific gravity of 3.12 at 15° C. and its density with respect to air is 5.5. It is soluble in water, one ml. of bromine dissolving in about 30 ml. of water. It is readily soluble in alcohol, ether, chloroform, benzene and many other organic solvents.

The fumes of bromine are highly irritating to the eyes and the respiratory tract, both upper and lower sections. It has an oxidizing action and elicits respiratory reflexes. Inhalation causes inflammation of the entire respiratory system with edema of the lungs after severe exposure.[7]

The least detectable odor of bromine is of the order of 3.5 parts per million; the least concentration causing irritation of the throat is 15.1 parts per million and 30.2 parts per million will cause coughing.[8] A concentration of 1000 parts per million will be lethal for human beings on exposures of a few minutes. Concentrations in the range of 40 to 60 parts per million are dangerous to life after exposures of 30 to 60 minutes. The maximum concentration that can be tolerated for an exposure of 60 minutes is 4 parts per million and the maximum that can be tolerated for several hours without serious symptoms is 1.0 part per million.

4. PHOSGENE

Phosgene was the most effective chemical war agent of 1914–1918 for more than 80 per cent of the gas fatalities were due to this substance. It was the second toxic agent used on a large scale.

Phosgene or carbonyl chloride, $COCl_2$, was called Collongite by the French; D-Stoff by the Germans and CG was the symbol assigned to it by the Americans and British. Phosgene is a colorless gas with an odor like that of musty hay. At low temperatures it is a liquid. It boils at 8.2° C.; freezes at −118° C.; has a specific gravity of 1.38 and a density with respect to air of 3.41, hence it is a comparatively heavy gas. It does not expand as readily as liquid chlorine. It has a low specific heat and a

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[7] Haggard, *J. Ind. Hyg.*, **5**, 397 (1923–4).

[8] Fieldner, Katz and Kinney, *U. S. Bur. Mines, Tech. Papers*, **248** (1921).

low heat of vaporization. It is the principal non-persistent chemical warfare agent. It dissolves readily in many organic solvents and is, itself, a solvent for many organic chemicals. It is hydrolyzed by water with the formation of hydrochloric acid.

Phosgene is over 10 times as toxic as chlorine; a concentration of 0.50 mg. per liter is lethal for an exposure of 10 minutes. Serious symptoms may not develop until several hours after exposure, for the immediate symptoms produced by even a fatal dose may be relatively mild, since phosgene elicits no marked respiratory reflexes; thus a person who appears to be but slightly gassed immediately following exposure, may become a serious casualty several hours later. Phosgene is a lung irritant and causes severe damage to the alveoli of the lungs. This is followed by pulmonary edema, resulting in asphyxiation. Inhalation of this gas produces catching of the breath, choking, immediate coughing, tightness of the chest, slight lachrymation, difficulty and pain in breathing and cyanosis. Its effects are probably due to hydrolysis and the formation of hydrochloric acid inside the body.

The most pronounced symptoms of phosgene poisoning are coughing with bloody sputum and weakness which may last for months.[9]

An atmosphere containing 1 part by volume of the gas in 6,000 may cause lung injuries in 2 minutes, 1 part in 30,000 is very dangerous, and 1 part in 200,000 is probably fatal for exposures of 30 minutes. The maximum permissible concentration for a prolonged exposure period is about 1 part per million, that is 0.004 mg. per liter.[10]

The least detectable odor of phosgene is 5.6 parts per million, the least concentration that affects the throat is 3.1 parts per million, the least concentration causing irritation of the eyes is 4.0 parts per million and the least concentration causing coughing is 4.8 parts per million.[11] A concentration of 0.02–0.05 per cent is lethal to most animals in a few minutes. A concentration of 0.0025 per cent is dangerous for exposures of 30 to 60 minutes. The maximum concentration to which animals can be exposed for several hours without serious symptoms is 0.0001 per cent or 1 part per million.[12]

5. DIPHOSGENE

Diphosgene, trichloromethylchloroformate, $ClCOOCCl_3$, was known as Perstoff to the Germans, Surpalite to the French and Diphosgene to the British. It is an oily, colorless liquid with an irritating, suffocating odor. It boils at 127° C.; has a specific gravity of 1.65 at 15° C.; a refractive

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[9] Berghoff, *Arch. Internal. Med.*, **24**, 678 (1919).

[10] *Dept. Sci. Ind. Research Brit.*, Leaflet No. 8 (1939) *Analyst*, **65**, 290 (1940).

[11] Fieldner, Katz and Kinney, *U. S. Bur. Mines*, *Tech. Papers*, **248** (1921).

[12] Sayers, DallaValle and Yant, *Ind. Eng. Chem.*, **26**, 1251 (1934).

index of 1.4566 at 22° C.; and its density referred to air is 6.9. At 20° C. it has a volatility of 26 mg. per liter. It is classed with the persistent agents, as its vapor will linger for about 30 minutes on open ground. It gets its name of diphosgene because it can decompose to form two molecules of phosgene. Diphosgene, if dry, has no corrosive action on metals and may be loaded directly into shell.

The toxicity of diphosgene is about the same as that of phosgene and, in all probability, it exerts its baneful effects on the human body by breaking down into phosgene in the body. It is a lung irritant but has somewhat greater lachrymatory powers than phosgene and consequently gives adequate warning at lower concentrations than does phosgene.

6. CHLOROMETHYLCHLOROFORMATE

Chloromethylchloroformate, that is, monochloromethylchloroformate, $ClCOOCH_2Cl$, is a colorless liquid of low viscosity with an irritating odor. It was used in combination with dichloromethylchloroformate by the French during World War I and was called Palite. The Germans used a similar agent and called it K-Stoff. It boils at about 107° C.; has a specific gravity of 1.47; is 4.5 times as heavy as air; and has a vapor pressure of 3.6 mm. Hg at 10° C. and 5.6 mm. Hg at 20° C. This agent is hydrolyzed by water at ordinary temperatures.

Chloromethylchloroformate is not considered a powerful lung irritant. It has very strong lachrymatory powers. The minimum concentration which produces involuntary weeping is 0.002 mg. per liter, while its threshold concentration is 0.05 mg. per liter.

7. CHLOROPICRIN

Chloropicrin is an ill-chosen name for this compound, for it implies some resemblance to picric acid, which it does not resemble. It probably derived its name from its formation by Stenhouse in 1848 from the action of picric acid on calcium hypochlorite. It was known as Vomiting Gas to the British; Aquinite to the French and Klop to the Germans. Its American symbol is PS.

Chloropicrin, trichloronitromethane, nitrochloroform, CCl_3NO_2, is a colorless, slightly oily liquid with a characteristic anise-like, sweet smell. It boils at 112° C.; and has a specific gravity of 1.651 at 20° /4° C. Its density with respect to air is 5.7. It has a refractive index of 1.4607 at 23° C. It has a higher vapor pressure than water; at 10° C. this pressure equals 10.9 mm. of mercury; at 20° C., it is 16.9 mm. and at 30° C., it is 30.5 mm. About 0.14 gram of chloropicrin is soluble in water at 25° C. but it is soluble in all proportions in alcohol and ether.

Chemically, chloropicrin is a stable compound. It is not hydrolyzed nor affected by cold water nor by cold mineral acids. Aqueous sodium hydroxide has no effect on it but it is slowly decomposed by alcoholic sodium hydroxide. It is rapidly decomposed by sodium ethylate, alcoholic sodium cyanide and sodium sulfite, and heat.

Chloropicrin is a toxic lung irritant and a strong lachrymatory agent. If it gets into the stomach it causes intense distress by producing nausea, vomiting, colic and diarrhea. Chloropicrin has good warning properties and is used industrially as a warning agent in commercial fumigants. Chloropicrin is more toxic than chlorine but less lethal than phosgene. A concentration of 2.0 mg. per liter for an exposure of 10 minutes is lethal as is a concentration of 0.8 mg. for an exposure of 30 minutes.[13]

TABLE 1

COMPARATIVE IRRITATING STRENGTH OF THE LUNG IRRITANTS

SUBSTANCE	MINIMUM IRRITATING CONCENTRATION		INTOLERABLE THRESHOLD	
	mg./l.	*ppm.*	*mg./l.*	*ppm.*
Chloropicrin	0.002–0.019	0.29–2.8	0.05	7.4
Ethylchlorosulfonate	0.002	0.34	0.05	8.5
Methylchlorosulfonate	0.002	0.37	0.03–0.04	5.6–7.5
Chloromethylchloroformate	0.002	0.38	0.05	9.5
Phenylcarbylamine chloride	0.003	0.42	0.03	4.2
Phosgene	0.005	1.2	0.02	4.9
Diphosgene	0.005	0.6	0.04	4.9
Dimethyl sulfate			0.05	9.7
Chlorine	0.01	3.6	0.1	35.

8. PHENYLCARBYLAMINE CHLORIDE

Phenylcarbylamine chloride, $C_6H_5NCCl_2$, was known as Green Cross I to the Germans. It is a colorless to pale yellow, oily liquid with an odor of onions. It boils at 210° C.; has a specific gravity of 1.35; yields a vapor 6.0 times as heavy as air. It is insoluble in water. It is soluble in organic solvents.

Phenylcarbylamine chloride was used as a lung irritant but it is also a nose, eye and throat irritant. A concentration of 0.03 mg. per liter equivalent to 4 parts per million is insupportable after 1 minute. A concentration of 0.003 mg. per liter or 0.4 parts per million will cause involuntary weeping. The lethal concentration for 10 minutes exposure is 0.5 mg. per liter. Concentrations of the order of 0.8 mg. per liter (110 ppm.) for exposures of 1–2 minutes will harm the respiratory organs.[14,15]

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[13] Prentiss, *Chemicals in War.* McGraw-Hill, New York, 1937.

[14] Flury, *Z. ges. exptl. Med.*, **13**, 567 (1921).

[15] Vedder, *Medical Aspects of Chemical Warfare.* Williams & Wilkins, Baltimore (1925).

9. DIMETHYL SULFATE

Dimethyl sulfate was used as a lung irritant, lachrymator and vesicant in the World War, 1914–1918.

Dimethyl sulfate, $(CH_3)_2SO_4$ is a colorless, oily liquid with a faint odor of onions. It boils with some decomposition at 188° C.; has a specific gravity of 1.335 at 15° C.; and a refractive index of 1.3874 at 20° C. It is almost insoluble in water but it is slowly decomposed by it with the formation of methyl sulfuric acid and methyl alcohol, or of sulfuric acid and dimethyl ether with further decomposition to methyl alcohol and formaldehyde. It yields a vapor which is 4.4 times as heavy as air.

TABLE 2

TOXICITY OF LUNG IRRITANTS[16]

SUBSTANCE	MINIMUM LETHAL CONCENTRATION 10 MINUTES EXPOSURE	
	mg./l.	*ppm.*
Phenyldibromoarsine	0.2	15.5
Phenyldichloroarsine	0.26	28.5
Dibromomethyl ether	0.4	48
Dichloromethyl ether	0.47	100
Ethyldichloroarsine	0.5	70
Phosgene	0.5	123
Trichloromethylchloroformate (diphosgene)	0.5	62
Dimethyl sulfate	0.5	97
Phenylcarbylamine chloride	0.5	70
Monochloromethylchloroformate	1.0	189.5
Ethylchlorosulfonate	1.0	169
Methylchlorosulfonate	2.0	375
Chloropicrin	2.0	297
Perchloromethyl mercaptan	3.0	395
Chlorine	5.6	1926

Dimethyl sulfate is not only a powerful lung irritant but it is also a lachrymator and vesicant. It affects all the mucous membranes, the conjunctiva, the respiratory system and the skin, through which it can be absorbed into the body. Inhalation of a sufficient quantity will cause edema of the lungs. Its caustic action on the skin is accompanied by an analgesic action which may last for a long time after exposure. A concentration of 0.50 mg. per liter is lethal for exposures of 10 minutes or more; hence this substance is about as toxic as phosgene.[16]

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[16] Prentiss, *Chemicals in War*. McGraw-Hill, New York, 1937.

10. METHYL AND ETHYLCHLOROSULFONATE

Methyl and ethylchlorosulfonates were generally used along with dimethyl sulfate. Ethylchlorosulfonate was known by the French as Sulvanite.

Methylchlorosulfonate, methylsulfuryl chloride, CH_3OSO_2Cl, is a viscous liquid, which boils at 133° C.; has a specific gravity of 1.51; has a vapor which is 4.5 times heavier than air.

It is a lung irritant and lachrymator. Its minimum lachrymatory concentration is 0.008 mg. per liter. Its intolerable threshold is 0.05 mg. per liter (7 parts per million). The lethal concentration for 10 minutes exposure is 2.0 mg. per liter. Death is caused by lung edema.

Ethylchlorosulfonate, ethylsulfuryl chloride, $C_2H_5OSO_2Cl$, is a colorless liquid which boils at 153° C.; has a specific gravity of 1.44; and has a vapor which is 5 times as heavy as air.

It is a lung irritant and lachrymator. Its minimum lachrymatory concentration is 0.005 mg. per liter, about 1 part per million. A concentration of 0.5 mg. per liter (9.3 parts per million) is intolerable after exposure of 1 minute.[17]

B. IRRITANTS

The irritants are chemical warfare agents which affect some organ of the body, causing intense distress but are seldom the cause of serious injury or death.

I. Lachrymators

Lachrymators, eye irritants, or tear gases, as they are commonly called, induce a copious flow of tears and intense, though temporary, eye pains even in very low concentrations. The smarting and watering of the eyes are also temporary and will cease if the person affected leaves the gassed area or wears an adequate respirator. In the liquid form, some of these gases resemble the vesicants or blister gases and at times are used to mask the presence of blister gases. All the tear gases used in World War I were halogen compounds. They are all rather closely related chemically.

1. ETHYLBROMOACETATE

Ethylbromoacetate, $CH_2BrCOOC_2H_5$, was used by the French in rifle grenades as early as August 1914. It is a colorless liquid boiling at 168° C. and has a specific gravity of 1.514 at 15/4° C. Its refractive index is 1.451 at 20° C.

It is a strong lachrymatory irritant and affects not only the eyes but all the mucous membranes. As little as 0.003 mg. per liter causes invol-

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[17] See Flury above.

untary weeping; 0.04 mg. per liter is a concentration intolerable to the eyes; 0.055 mg. per liter or 8 parts per million for exposures of 1 minute are intolerable, and a concentration of 2.3 mg. per liter is lethal for exposures of 10 minutes. Since its volatility is 21.0 mg. per liter at 20° C., lethal concentrations are practical.[18, 19]

2. ETHYLIODOACETATE

Ethyliodoacetate, $CH_2ICOOC_2H_5$, was given the symbol KSK by the British. It is a colorless, oily liquid with a specific gravity of 1.8. It boils at 178–180° C. with some decomposition and the liberation of iodine. Its vapor pressure is 0.54 mm. Hg at 20° C. It is a persistant war agent.

Ethyliodoacetate is a stronger irritant and lachrymator than ethylbromoacetate. A concentration of 0.0014 mg. per liter will cause involuntary weeping; a concentration of 0.0035 mg. per liter equivalent to a concentration of 0.4 parts per million, will disable a person; a concentration of 0.015 mg. per liter is intolerable; a concentration of 0.17 mg. per liter or 20 parts per million will cause serious injury if breathed for 1–2 minutes; a concentration of 1.5 mg. per liter for 10 minutes exposure is lethal.

3. METHYLCHLOROFORMATE

Methylchloroformate $ClCOOCH_3$, is a colorless liquid which boils at 71.4° C.; has a specific gravity of 1.2; and yields a vapor 3.9 times heavier than air. It is not hydrolyzed by cold water but is hydrolyzed by hot water with the formation of carbon dioxide and methanol.

Methylchloroformate is a strong lachrymator and is used as a warning agent in fumigations with hydrocyanic acid.

4. BROMOACETONE

Bromoacetone, called B-Stoff by the Germans, Martonite by the French and BA by the British and Americans, was the most widely used lachrymatory agent in the World War of 1914–1918. Bromoacetone, $CH_2BrCOCH_3$, is a colorless liquid which boils at 135–136° C.; it has a specific gravity of 1.6 and has a vapor density 4.7 times that of air. It has a vapor pressure of 9 mm. Hg at 20° C. It is slightly soluble in water, slightly soluble in alcohol but readily soluble in acetone. It decomposes and polymerizes on standing.

Bromoacetone is a strong lachrymator but liquid bromoacetone is also a vesicant, forming blisters which heal rapidly but are very painful. A concentration of 0.3 parts per million, or 0.0015 mg. per liter, is sufficient to cause involuntary weeping; a concentration of 0.01 mg. per liter or 1.8 parts per million will incapacitate men and a concentration of 0.56

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[18] Flury and Zernik, *Schaedliche Gase*. Springer, Berlin, 1931.

[19] Prentiss, *Chemicals in War*. McGraw-Hill, New York, 1937.

mg. per liter or 100 parts per million is distinctly injurious after 1 to 2 minutes exposure.[20] A concentration of 0.010 mg. per liter is intolerable and a concentration of 3.2 mg. per liter is lethal after 10 minutes exposure. This concentration can easily be obtained with this agent, for its volatility at 20° C. is 75 mg. per liter; hence bromoacetone can act as a lethal agent.[21]

5. BROMOMETHYLETHYL KETONE

Bromomethylethyl ketone, $CH_2BrCOC_2H_5$, was used as a substitute for bromoacetone because acetone was too valuable for other purposes. The Germans called it Bn-Stoff and the French, Homomartonite. It is a pale yellowish or colorless liquid which boils at about 145–146° C. with some decomposition. It has a specific gravity of 1.43 and a vapor which is 5.2 times as heavy as air. It is slightly soluble in water.

Bromomethylethyl ketone is only slightly weaker than bromoacetone as a lachrymator. It resembles bromoacetone closely in its other properties also. The lowest concentration causing involuntary weeping is 0.011 mg. per liter or 1.8 parts per million; a concentration of 0.0126 mg. per liter or 2 parts per million will incapacitate a person; a concentration of 0.016 mg. per liter is intolerable; a concentration of 1.26 mg. per liter is distinctly injurious after exposures of 1 to 2 minutes and a concentration of 2.0 mg. per liter is lethal for exposures of 10 minutes or more.[20, 21]

6. CHLOROACETOPHENONE

Chloroacetophenone is called under the American system CN. It was not used in the World War, 1914–1918, because it was not developed until the end of that war. Chloroacetophenone, $C_6H_5COCH_2Cl$, is a colorless, crystalline solid with an odor resembling apple or locust blossoms in very low concentrations. It melts at 59° C.; has a specific gravity of 1.324 at 15° C.; has a low vapor pressure of 0.013 mm. Hg at 20° C.; boils at 247° C.; and has a vapor density of 5.3 referred to air. It is insoluble in water but is soluble in alcohol, ether, carbon disulfide and other organic solvents.

Chloroacetophenone is a strong lachrymator but in addition has a powerful irritant action on the upper respiratory tract. It is a skin irritant also and produces a burning and itching sensation which lasts for a long time unless the clothing upon which it has fallen is changed immediately for other clothes. These effects are transitory, however, unless very high concentrations have been inhaled. Chloroacetophenone is about equal to bromobenzyl cyanide in lachrymatory powers so that a concentration of 0.0003 mg. per liter will induce tears; a concentration of 0.0045 mg. per liter is intolerable and a concentration of 0.85 mg. per liter for exposures of 10 minutes is lethal.[21]

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[20] Flury and Zernik, *Schaedliche Gase.* Springer, Berlin, 1931.

[21] Prentiss, *Chemicals in War.* McGraw-Hill, New York, 1937.

a) CNS Tear Gas Solution

CNS is the U. S. Chemical Warfare Service symbol for a tear gas solution containing 23.2 per cent of chloroacetophenone, 38.4 per cent of chloropicrin and 38.4 per cent of chloroform. It is a colorless liquid changing to a colorless gas. Its crystallization point is 1.4° C.; it has a specific gravity of about 1.5 and a vapor density of about 5. It has a sweetish, anise-like odor resembling that of fly paper. It is a lachrymator and respiratory irritant which causes piercing irritation of the eyes, profuse tears, followed by nausea and vomiting. It is a semi-persistent harassing agent for it lingers about 1 hour in the open, and 2 hours in the woods during summer while in winter it will persist for 6 hours in the open and about a week in the woods. Its minimum irritating concentration for an exposure of 3 minutes is 0.02 mg. per liter. Exposures for 30 minutes to concentrations of the order of 3.8 mg. per liter may be fatal.

b) CNB Tear Gas Solution

CNB is the U. S. Chemical Warfare Service symbol for a tear gas solution containing 10 per cent of chloroacetophenone, 45 per cent of carbon tetrachloride and 45 per cent of benzene. It is a colorless liquid which vaporizes to a colorless gas. It has a specific gravity of 1.14 and a crystallization point of −7° C. Its odor resembles that of benzene. It is a lachrymator causing a physiological response entirely analogous to that of chloroacetophenone.

7. BENZYL BROMIDE AND XYLYL BROMIDE

Benzyl bromide and xylyl bromide were both called T-Stoff by the Germans and benzyl bromide was called Cyclite by the French. Both are strong lachrymators. Benzyl bromide, $C_6H_5CH_2Br$, is a colorless liquid, which boils at 201° C.; has a specific gravity of 1.44. It has a pleasant aromatic odor resembling watercress. It has a vapor pressure of 2.0 mm. Hg at 20° C. and a vapor which is 6 times as heavy as air.

Xylyl bromide is really a mixture of isomeric bromides and xylylene bromides. The mixture used for the war gas was a black liquid having a pungent aromatic odor and a boiling range of 210–220° C. It had a specific gravity of 1.4 and its vapor was 8.5 times as heavy as air. It has an odor resembling lilacs or elder leaves and for this reason was called Elder gas by the British.

Benzyl bromide does not only act upon the eyes but is an irritant for all the mucous membranes. In higher concentrations it causes salivation and nausea. The minimum concentration that will produce irritation is 0.004 mg. per liter; a concentration of 0.05–0.06 mg. per liter (7–8 parts per million) is intolerable; its lethal concentration is 4.5 mg. per liter for exposures of 10 minutes.[22, 23]

Xylyl bromide is much more irritating than benzyl bromide and a concentration as low as 0.00027 mg. per liter can be detected by sensitive individuals. Its minimum lachrymatory concentration is 0.0018 mg. per liter; a concentration of 0.0038 mg. per liter equivalent to 5 parts per million will incapacitate an unprotected person within a few seconds; a concentration of 0.015 mg. per liter is intolerable after 1 minute and a concentration of 5.6 mg. per liter is lethal for exposures of 10 minutes or longer. Thus, while xylyl bromide has stronger warning properties, it is slightly less toxic than benzyl bromide.

8. BROMOBENZYL CYANIDE

Bromobenzyl cyanide, $C_6H_5CHBrCN$, was called Camite by the French, symbolized CA by the Americans and BBC by the British. It was the most powerful lachrymator used in the World War, 1914–1918. Bromobenzyl cyanide is a yellowish-white, crystalline solid with an odor resembling soured fruit. It melts at 25° C. to form a brownish oily liquid which has a specific gravity of 1.47 and a boiling point of 225° C. Its vapor has a density of 6.8 compared to air and it has a vapor pressure of 0.012 mm. Hg at 20° C.; at 30° C. the vapor pressure is 0.028 mm. Bromobenzyl cyanide is only slightly soluble in water but it is easily soluble in alcohol, ether, chloroform, acetone and most common organic solvents. It is very soluble in phosgene, chloropicrin and benzyl cyanide. It is a persistent war gas.

Bromobenzyl cyanide is a very strong eye irritant. It also causes a burning sensation in the mucous membranes. It is seven times as powerful a lachrymator as bromoacetone and can be detected in concentrations as low as 1 part in 100,000,000 which is equivalent to 0.00087 mg. per liter. The minimum irritating effect on the eyes is 0.00015 mg. per liter; the least concentration causing lachrymation is 0.0003 mg. per liter; a concentration of 0.0008 mg. per liter is intolerable and 0.09 mg. per liter is lethal for exposures of 30 minutes but, because of its low volatility, this concentration cannot be obtained in the field.[24]

9. SULFUR MONOCHLORIDE

Sulfur monochloride, S_2Cl_2, is a reddish yellow liquid which boils at 138° C.; and has a specific gravity of 1.678. It is decomposed by water

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[22] Flury and Zernik, *Schaedliche Gase.* Springer, Berlin, 1931.

[23] Vedder, *The Medical Aspects of Chemical Warfare.* Williams & Wilkins, Baltimore, 1925.

[24] Prentiss, *Chemicals in War.* McGraw-Hill, New York, 1937.

with the formation of sulfur dioxide, sulfur and hydrochloric acid. It is soluble in carbon disulfide, ether, benzene and other organic solvents. It is a solvent for sulfur and fats.

Sulfur monochloride has a suffocating, nauseating and pungent odor. It induces lachrymation and is an irritant for the mucous membranes of the nose, throat and especially the eyes. The compound is of questionable toxicity but because it readily decomposes, as mentioned above, into sulfur dioxide and hydrochloric acid, it may cause injury because of the presence of these compounds.

TABLE 3

COMPARATIVE STRENGTH OF LACHRYMATORS

SUBSTANCE	MINIMUM IRRITATING CONCENTRATION		INTOLERABLE THRESHOLD	
	mg./l.	*ppm.*	*mg./l.*	*ppm.*
Bromobenzyl cyanide	0.00015–0.003	0.019–0.037	0.005–0.03	0.6–3.7
Chloroacetophenone	0.0003	0.048	0.0045–0.012	0.7–1.9
Brominated ketones	0.0012			
Ethyliodoacetate	0.0014	0.16	0.015	1.7
Bromoacetone	0.0015	0.27	0.01	1.8
Bromomethylethyl ketone	0.0016	0.26	0.01	1.6
Xylyl bromide	0.0018	0.24	0.015	2.0
Chloropicrin	0.002–0.019	0.29–2.8	0.05	7.4
Benzyl iodide	0.002	0.22	0.025–0.03	2.8–3.4
Chloromethylchloroformate	0.002	0.38	0.05	9.4
Methylchlorosulfonate	0.002	0.37	0.03–0.04	5.6–7.5
Ethylchlorosulfonate	0.002	0.34	0.05	8.5
Dichloromethylchloroformate			0.075	11.3
Cyanogen chloride	0.0025	1.0	0.05	19.5
Phenylcarbylamine chloride	0.003	0.42	0.03	4.2
Ethylbromoacetate	0.003–0.01	0.44–1.5	0.04	5.9
Methylchloroformate			0.045	11.6
Benzyl bromide	0.004	0.57	0.05–0.06	7–8
Cyanogen bromide	0.006	1.38	0.085	19.6
Acrolein	0.007	3.06	0.05	21.9
Chloroacetone	0.018	4.75	0.1	26.5
Iodoacetone	0.012	1.59		
Bromopicrin	0.03	2.46		

10. THIONYL CHLORIDE

Thionyl chloride, sulfurous oxychloride, $SOCl_2$, is used in the preparation of chlorinated substances, among which may be mentioned mustard gas. It is a colorless, strongly refractive liquid, which fumes on contact with air and has a suffocating odor. It boils at 78–79° C.; has a specific gravity of 1.638; and a refractive index of 1.527 at 10° C. It decomposes in water with the formation of hydrochloric acid, and sulfur dioxide. It is soluble in sulfur, benzene and chloroform but decomposes in acids, alkali and alcohol.

It is an eye irritant and because of its decomposition into hydrochloric acid and sulfur dioxide exerts the harmful effects of those substances on the human body.

11. SULFURYL CHLORIDE

Sulfuryl chloride, sulfuric oxychloride, SO_2Cl_2, is used in the preparation of chlorosulfonates, for instance, methyl and ethyl chlorosulfonates. During the World War, 1914–1918, it was used in combination with phosgene, chloropicrin and cyanogen chloride to make the toxic gases visible. It was also used as a smoke agent.

TABLE 4

TOXICITY OF LACHRYMATORS

SUBSTANCE	MINIMUM LETHAL CONCENTRATION 10 MINUTES EXPOSURE	
	mg./l.	*ppm.*
Acrolein	0.35*	153
Bromobenzyl cyanide	0.35	43.4
Phenylcarbylamine chloride	0.50*	63.5
Chloroacetophenone	0.85	135
Ethyliodoacetate	1.5*	171
Iodoacetone	1.9	252
Chloropicrin	2.0*	297
Bromomethylethyl ketone	2.0*	324
Ethylbromoacetate	2.3*	337
Chloroacetone	2.3	607
Benzyl iodide	3.0	337
Bromoacetone	3.2*	573
Benzyl bromide	4.5	643
Xylyl bromide	5.6	740

* Volatilities exceed minimum lethal concentration, hence fatal concentrations may be produced in the field.

Prentiss, *Chemicals in War*. McGraw-Hill, New York, 1937.

Sulfuryl chloride is a colorless, fuming liquid with a pungent odor. It boils at 69° C.; has a specific gravity of 1.667 and a refractive index of 1.444 at 20° C. It is decomposed by water with the formation of sulfuric acid and hydrochloric acid, the reaction being very rapid with warm water. It is soluble in acetic acid and benzene and in the war gases mentioned above. Its ability to be used as a smoke depends on its hydrolysis by the water vapor of the air.

Its physiological effect is due no doubt to its hydrolytic products and so it has an irritating effect.

12. MONO AND DICHLOROFORMOXIME

Monochloroformoxime, ClCH:NOH, is a crystalline solid which is soluble in water and in many organic solvents but is almost insoluble in petroleum ether and only slightly soluble in carbon disulfide. It sublimes at ordinary temperatures.

Dichloroformoxime, phosgene oxime, $Cl_2C:NOH$, is a crystalline solid with a penetrating, unpleasant odor. It melts at 39–40° C.; boils at 129° C. It is soluble in water and in many organic solvents.

Both mono- and dichloroformoxime possess strong lachrymatory powers. They are also both vesicants. They are closely related to fulminic acid. They were not used in the World War, 1914–1918 but have been suggested as possible chemical warfare agents.

II. Toxic Smokes

When toxic smokes were first used in the World War, 1914–1918, it was not known how to disperse them in a fine state of division, consequently they were only coarsely dispersed and in this state caused intense sneezing as their primary effect. Because they were able to produce this symptom they were termed *Sternutators.* Under more modern classification they are termed toxic smokes because they produce their baneful effect by their finely dispersed state and not by the formation of a vapor. All the toxic smokes are derivatives of arsine, AsH_3.

Nose irritants or sneezing gases induce intense pain and irritation in the nose, mouth, throat, chest and eyes. The inhalation of low concentrations causes sneezing, coughing, watering of the eyes and headache, which are often followed by violent nausea, vomiting, acute mental distress and temporary physical disability. They are unlikely to cause serious injury or death.

1. DIPHENYLCHLOROARSINE

Diphenylchloroarsine, $(C_6H_5)_2AsCl$, was termed Clark I by the Germans and was given the symbols DA by the Americans. It is a colorless, crystalline solid when pure but has a yellowish color when impure. The pure compound melts at about 45° C. and the impure material at about 40° C. It has a boiling point of 383° C. at 760 mm. Hg in an atmosphere of carbon dioxide. Its specific gravity is 1.58; its vapor pressure at normal temperatures is negligible. It is slightly soluble in water but is readily soluble in absolute alcohol, kerosene, benzene, and is very soluble in carbon tetrachloride and phosgene. It has an odor resembling that of shoe polish.

Since diphenylchloroarsine is a solid and has a negligible vapor pressure, it cannot produce its physiological effect through the vapor state. It is dispersed by heating to form a dust and in that form produces at first a tickling sensation in the nose, followed by sneezing, then coughing, choking and headache, pains in the chest, nausea and vomiting. Low concentrations first attack the upper respiratory passages, but, on prolonged exposure, have their effect on the lower respiratory organs also. Higher concentrations lead to nervous disturbances which are evidenced by twitching, unsteady gait and similar manifestations.

One part of diphenylchloroarsine dust in 25,000,000 parts of air, equivalent to 0.0005 mg. per liter, can produce marked irritation of the nose and throat. A concentration range of 0.001–0.002 mg. per liter is unbearable for a normal person and will incapacitate an improperly protected person in a few seconds. A concentration of 0.01 mg. per liter will cause retching; a concentration of 1.5 mg. per liter is lethal for exposures of 10 minutes and concentrations of 0.6 mg. per liter after 30 minutes exposure. Since concentrations of this order cannot be obtained in the vapor state, it is difficult to obtain lethal concentrations, but the inhalation of sufficient of the dust can also be lethal.

TABLE 5

COMPARATIVE STRENGTH OF TOXIC SMOKES

SUBSTANCE	MINIMUM IRRITATING CONCENTRATION		INTOLERABLE THRESHOLD		LETHAL CONCENTRATION (DOGS) 30 MINUTES EXPOSURE	
	mg./l.	*ppm.*	*mg./l.*	*ppm.*	*mg./l.*	*ppm.*
Diphenylcyanoarsine	0.00005–0.0001	0.005–0.01	0.00025	0.024		
Diphenylaminechloroarsine	0.0001	0.009	0.004	0.035	0.65	5.7
Diphenylchloroarsine	0.0001	0.009	0.001–0.007	0.092–0.18	0.6	5.5

2. DIPHENYLAMINECHLOROARSINE

Diphenylaminechloroarsine, phenarsazine chloride, Adamsite, was symbolized by the Americans DM. When pure, diphenylaminechloroarsine, $NH:(C_6H_4)_2:AsCl$, is a canary yellow crystalline solid, but is dark green in color when impure. It melts at 195° C. and has a specific gravity of 1.65. Its vapor pressure is practically negligible at ordinary temperatures but when heated or distilled, it passes into the air in the form of minute particles of the order of 10^{-4} to 10^{-5} cm. in diameter. It is insoluble in water, is insoluble in phosgene, is but slightly soluble in carbon tetrachloride and moderately soluble in absolute alcohol, kerosene and benzene. It is, however, somewhat soluble in chloroform, glacial acetic acid and hot mustard gas.

The physiological effects caused by diphenylaminechloroarsine are similar to those produced by diphenylchloroarsine. It irritates the mucous membranes of the nose and throat in concentrations of 1 part of the dust in 30,000,000 parts of air, that is 0.00038 mg. per liter. The lower respiratory tract is affected at concentrations of the order of 0.005 mg. per liter. A concentration of 0.4 mg. per liter is lethal for most animals. Ten minutes exposure to a concentration of 3.0 mg. per liter is lethal for human beings as is a concentration of 0.65 mg. per liter for exposures of 30 minutes duration.

3. DIPHENYLCYANOARSINE

Diphenylcyanoarsine, (Clark II, German; CD, British; CDA, American) $(C_6H_5)_2AsCN$, was used to replace and in conjunction with diphenylchloroarsine. It is a colorless, crystalline solid in the pure state. It melts at 31.5° C.; has a specific gravity of 1.45; and boils at about 350° C. with some decomposition. It yields a vapor which is 8.8 times as heavy as air. It is difficultly soluble in water and is not readily hydrolyzed. It is not as volatile as diphenylchloroarsine; at 20° C. its volatility is 0.1 mg. per cubic meter. It forms a smoke readily.

The physiological response of diphenylcyanoarsine is entirely analogous to that of diphenylchloroarsine. The lowest concentration that is detectable is 0.000005 mg. per liter, according to Flury.[25] The lowest irritant concentration is 0.0001 mg. per liter. A concentration of 0.00025 mg. per liter is intolerable. A concentration of 0.0025 mg. per liter produces marked irritation and pains deep in the breast. The lethal concentration is 1.0 mg. per liter but this is practically impossible to obtain in the field. Inhalation for but 1 or 2 minutes of a concentration 2.8 mg. per liter will harm the respiratory tract.[26]

III. Labyrinthic War Gases

These war gases appear to have an effect on the semicircular canals of the inner ear. They disturb the sense of equilibrium and thus produce staggering and vertigo. They are also lung irritants. They did not play an important role in World War I. The principal agents of this group are dichloromethyl ether and dibromomethyl ether.

1. DICHLOROMETHYL ETHER

Dichloromethyl ether, *sym.*-dichloromethyl ether, $ClCH_2OCH_2Cl$, is a colorless liquid with a suffocating odor. It boils at 106° C.; has a specific

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[25] Flury, *Z. ges. exptl. Med.*, **13**, 550 (1921).

[26] Vedder, *Medical Aspects of Chemical Warfare.* Williams & Wilkins, Baltimore, 1925.

gravity of 1.315 at 20/4° C.; and a refractive index of 1.4346 at 20° C. It is unstable in moist air and is decomposed into hydrochloric acid and formaldehyde; hence is not an efficient chemical agent. It is used not only as a war gas but as a solvent for other chemical agents.

Dichloromethyl ether is distinctly irritating in a concentration of 0.0003 per cent by volume which is equivalent to 3 parts per million. A concentration of 0.01 per cent will incapacitate a person in a few seconds and an exposure of 1 to 2 minutes may produce a fatal lung injury.[27, 28]

C. VESICANTS

Vesicants or blister gases are chemical warfare agents which are readily absorbed or dissolved by the interior or exterior tissues of the body with subsequent production of inflammation, burns and destruction of tissue. Prolonged exposure to the vapors of these agents may cause serious eye injuries and if the liquid substance gets into the eyes, blindness may result. The physiological action of these agents is insidious. While Lewisite has some lachrymatory warning power, mustard gas has practically none. Consequently one may be exposed to its vapors without realizing it until serious damage has been done.

1. DICHLOROETHYL SULFIDE, MUSTARD GAS

Dichlorodiethyl sulfide, β, β-dichlorodiethyl sulfide, $(CH_2ClCH_2)_2S$, was known as Mustard Gas, its British and common name, as Lost and also as Yellow Cross by the Germans. Its American symbols are HS and the French call it Yperite. As the name mustard gas indicates, this substance has vesicant and irritant properties. It was first used by the Germans in July 1917 and produced a higher rate of casualties than any other war gas.

The following are the chief physical properties of mustard gas. It is a heavy, oily liquid and, when pure, it is nearly odorless and colorless. In its impure state it is dark-colored and has a pungent garlic-like or horseradish-like odor. It melts in the pure state at 14° C. but in the impure state its melting point ranges from 4.6–14° C. It boils at 228° C. with some decomposition. It has a low vapor pressure ranging from 0.026 mm. at 0° C. to 0.15 mm. at 30° C. Its volatility is correspondingly low ranging from 0.25 mg. per liter at 0° C. to 1.4 mg. per liter at 30° C. Its vapor is 5.5 times as heavy as air. It is practically insoluble in water but is soluble in hydrocarbons, carbon tetrachloride, carbon disulfide, monochlorobenzene and other organic solvents. It dissolves rubber.

Mustard gas is a stable compound at ordinary temperatures. It decomposes above 150° C. and at 500° C. the decomposition is complete. Mustard is slowly hydrolyzed by water with the formation of thiodiglycol,

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[27] Flury and Zernik, *Schaedliche Gase.* Springer, Berlin, 1931.

[28] Schrenk, Patty and Yant, *U. S. Pub. Health Repts.*, **48**, 1389 (1933).

which is non-toxic and hydrochloric acid, which is toxic. The hydrolysis is more rapid at higher temperatures. Hypochlorites and bleaching powder react violently with mustard gas. Because of its low volatility, this war gas is a persistent agent.

Mustard gas is not only a vesicant and skin and eye irritant but it is also lung irritant. The symptoms produced by exposure to this gas are delayed and usually do not appear until from two to four hours afterwards unless direct contact with the liquid substance occurs. The symptoms produced are burning of the eyes, followed by conjunctivitis or inflammation; burning of the skin surface, especially of the moist areas, followed by discoloration and blistering; a hoarse cough, expectoration, and severe pain in the chest. Inflammatory destruction of the mucous membranes of the entire respiratory tract, especially of the trachea and bronchi, with the possibility of development of pneumonia.[29] Berghoff[30]

TABLE 6

PHYSIOLOGICAL RESPONSE OF MEN TO MUSTARD GAS

PPM.	MG./L.	TIME OF EXPOSURE	RESPONSE	REFERENCE BELOW
0.077	0.0005	10–25 min.	May harm the eyes and skin	(1)
0.15	0.001	1–2 hrs.	Conjunctivitis	(2)
		8–10 hrs.	Disables	(1)
0.18	0.0012	45 min.	After a delay of 12 hrs. eyes show effects, after 2 days skin shows effects	(1)
0.18	0.0013		Least detectable odor	(2)
0.38–0.77	0.0025–0.005	30–60 min.	Irritates skin of sensitive persons	(1)
1.0	0.0065	60 min.	Lungs seriously affected	(3)
			Endurable for 30 to 60 min.	(4)
11.	0.07	30 min.	Lethal	(3)
15.	0.1	30–60 min.	Lethal	(4)
20	0.13	5–10 min.	Lethal	(4)
15.4–20.8	0.1–0.2	few sec.	Itching of tender parts of skin persists for weeks	(5)

(1) Reed, *J. Pharmacol.*, **15,** 71 (1920).

(2) Prentiss, *Chemicals in War*, McGraw-Hill, New York, 1937.

(3) Vedder, *Medical Aspects of Chemical Warfare*, Williams & Wilkins, Baltimore, 1925.

(4) Leschke *Clinical Toxicology*, William Wood, Baltimore, 1934.

(5) Flury and Wieland, *Z. ges. exptl. Med.*, **13,** 370 (1921). Flury and Zernik, *Schaedliche Gase*, Springer, Berlin, 1931.

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[29] U. S. Chem. Warfare Service, *Handbook First-Aid Treatment for Injuries from Chemical Agents*. 1931.

[30] Berghoff, *Arch. Internal. Med.*, **24,** 678 (1919).

states that the most pronounced early symptom of mustard gas poisoning is that of hemorrhage and bleeding from the nose. The physiological response of men to mustard gas is tabulated in Table 6.

2. CHLOROVINYLDICHLOROARSINE, LEWISITE

β-Chlorovinyldichloroarsine $ClCH{:}CHAsCl_2$ has the American symbol M1. It was not used in the World War of 1914–1918 because it was developed by Americans late in the war. M2 is the symbol used to designate β, β-dichlorovinylchloroarsine, $(ClCH{:}CH)_2AsCl$ and M3 for the tertiary compound, trichlorovinylarsine, $(ClCH{:}CH)_3As$. The primary and secondary Lewisites are both highly toxic agents but the tertiary compound is of little value as a war agent. The term Lewisite, unqualified, is used to designate the primary compound.

Lewisite is an oily, colorless to slightly yellow liquid when pure. The technical preparation is a dark, green, oily liquid with an odor resembling geraniums. It boils at 190° C.; has a specific gravity of about 1.89; it yields a vapor which is 7.1 times as heavy as air. It has a low vapor pressure, namely 0.087 mm. of mercury at 0° C. and 0.77 mm. at 30° C. It is insoluble in water but is soluble in organic solvents. Lewisite is less persistent than mustard gas, since its vapor pressure and volatility are both higher. It hydrolyzes readily and is easily decomposed by ammonia, aqueous alkali solution and bleaching powder.

Lewisite is not only a vesicant and lung irritant like mustard gas but in addition is a systemic poison, inasmuch as it contains arsenic. It can be absorbed into the body through the lungs or directly through the skin. From this point of view it is a more effective agent than mustard. From tactical points of view it is a less effective agent.

The symptoms produced by Lewisite are similar to those produced by mustard gas, but are of a more severe nature. This chemical war agent acts immediately as a lachrymator and as a lung irritant. Its vesicant action is much more rapid than that of mustard gas for demarcation of the affected area is plain at the end of 15 minutes after Lewisite has come in contact with the skin. Both the liquid and vapor cause irritation of the lungs, inflammation of the eyes and skin burns. Retching, vomiting, and excessive salivation also occur. The immediate lung symptoms from Lewisite are not very marked but the skin burn appears as a grayish discoloration within 30 minutes after exposure to the liquid.[31]

Since Lewisite undergoes hydrolysis to yield chlorovinylarsine oxide, its hydrolytic products are also poisonous.

The least detectable odor is given by a concentration of 0.014 mg. per

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[31] U. S. Chem. Warfare Service, *Handbook First-Aid Treatment for Injuries from Chemical Agents.* 1931.

liter. This is far above the minimum irritating concentration of Lewisite, namely, 0.0008 mg. per liter. Its minimum vesicant concentration is 0.334 mg. per liter. A concentration of 0.12 mg. per liter is fatal for exposures of 10 minutes and an exposure to 0.048 mg. per liter is lethal after 30 minutes. The minimum blistering concentration is only one-tenth of the saturation concentration at 20° C.[32]

3. METHYLDICHLOROARSINE

Methyldichloroarsine, CH_3AsCl_2, is a colorless liquid with a characteristic odor. It boils at 132–133° C.; has a specific gravity of 1.84; and yields a vapor which is 5.5 times as heavy as air. Its vapor pressure at 0° C. is 2.2 mm. of mercury and at 20° C. it is 8.5 mm. It is slightly soluble in water: 0.1 gram in 100 ml. and is readily hydrolyzed. It is soluble in organic solvents.

Table 7

Comparative Strength of Vesicants

	MINIMUM IRRITATING CONCENTRATION		INTOLERABLE THRESHOLD		LETHAL CONCENTRATION	
	mg./l.	*ppm.*	*mg./l.*	*ppm.*	*mg./l.*	*ppm.*
Lewisite	0.001–0.008	0.12–0.94	0.048	5.6	0.05	6
Phenyldichloroarsine			0.016	1.8	[0.1]	[13]
Ethyldichloroarsine	0.001–0.0015	0.14–0.21	0.01	1.4	0.1	14
Methyldichloroarsine	0.001	0.15	0.025	3.8	0.12	16
Mustard gas*					0.07	11

* Practically no initial irritating effect.

Methyldichloroarsine is a toxic irritant, a lung irritant, a vesicant and a systemic poison. Inhalation of the vapor or dust produces a burning sensation along the entire respiratory tract and a gasping for breath. Coughing, nasal discharge, frothing at the mouth and later bloody expectoration are produced. Almost simultaneously, if the vapor is not concentrated, lachrymation, together with burning and marked swelling of the eyes are produced. Ulceration of the eyes may follow later. Exposure to either the liquid or vapor causes skin burns of varying degrees.[33] The symptoms all appear within an hour after exposure.

A concentration of 0.025 mg. per liter for a 1 minute exposure is the intolerable threshold. A concentration of 0.002 mg. per liter causes sneezing and pains in the chest; 0.009 mg. per liter has a sternutory action.

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[32] Prentiss, *Chemicals in War*. McGraw-Hill, New York, 1937.

[33] U. S. Chem. Warfare Service, *Handbook First-Aid Treatment for Injuries from Chemical Agents*, 1931.

The lethal concentration for 10 minutes exposure is 0.56 mg. per liter and for 30 minutes exposure is 0.12 mg. per liter.[34]

4. ETHYLDICHLOROARSINE

Ethyldichloroarsine, $C_2H_5AsCl_2$, was called Dick and Green Cross 3 by the Germans. Its American symbol is ED. The pure product is a clear, rather oily liquid with a pleasant fruity odor. It boils at 156° C.; has a specific gravity of 1.7 and yields a vapor which is 6.5 times as heavy as air. It is somewhat soluble in water: 0.1 gram in 100 ml. Water also hydrolyzes it. It is readily soluble in many organic solvents.

Ethyldichloroarsine is a lung irritant, a toxic smoke, a vesicant and a systemic poison. The physiological effects may be summarized as follows: A concentration of 0.00017 per liter (0.024 parts per million) for exposures of 5 minutes gives no warning by odor or irritation. The minimum warning concentration due to odor is 0.00087 mg. per liter (0.12 parts per million) for exposures of 5 minutes. This concentration irritates the nose slightly. Five minutes exposure to a concentration of 0.0017 mg. per liter produces strong nose and mouth irritation. Five minutes exposure to a concentration of 0.0085 mg. per liter produces a strong irritation which lasts 24 hours. A few breaths of a concentration of 0.034 mg. per liter (4.8 parts per million) is unbearable. The intolerable threshold is 0.005–0.007 mg. per liter (0.7–1.0 parts per million).[35] A concentration of 0.014 mg. per liter is disabling within a few minutes and a concentration of 0.035 mg. per liter breathed for 1–2 minutes will affect the respiratory passages.[36] A concentration of 0.5 mg. per liter is lethal for exposures of 10 minutes and 0.1 mg. per liter is lethal after 30 minutes exposure.[37]

5. PHENYLDICHLOROARSINE

Phenyldichloroarsine, $C_6H_5AsCl_2$, was used by the Germans as a solvent for diphenylcyanoarsine, Clark II. It was also used by the French in a mixture with diphenylchloroarsine known as Sternite. It is a viscous liquid which boils at 252° C., has a specific gravity of 1.64 and yields a vapor which is 7.7 times as heavy as air. Phenyldichloroarsine is used as a 1 per cent solution in medium and heavy petroleum distillates for a wood preservative.[38] It is insoluble in water but is readily hydrolyzed. It is soluble in most organic solvents. It has a very low vapor pressure, namely, 0.015 mm. Hg at 15° C.

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[34] Prentiss, *Chemicals in War.* McGraw-Hill, New York, 1937.

[35] Flury, *Z. ges. exptl. Med.*, **13**, 541 (1921).

[36] Vedder, *Medical Aspects of Chemical Warfare.* Williams & Wilkins, Baltimore, 1925.

[37] Prentiss, *Chemicals in War.* Mc-Graw Hill, New York, 1937.

[38] Dudley and Jones, *U. S. Pub. Health Repts.*, **53**, 338 (1938).

Phenyldichloroarsine is a lung irritant. It has vesicant properties which are less severe than mustard gas but are greater than methyldichloroarsine.[39] It is impossible to tolerate a concentration of 0.0164 mg. per liter for more than 1 minute.[40] The lethal dose for guinea pigs is 8–10 mg. per kilogram of body weight. It is also a general protoplasmic poison.

Table 8

Toxicity and Comparison of Vesicants*

SUBSTANCE	MINIMUM LETHAL CONCENTRATION 10 MINUTES EXPOSURE		ORDER OF SKIN-IRRITANT EFFICIENCY
	mg./l.	*ppm.*	
Lewisite	0.12	14.2	2
Mustard gas	0.15	23.1	1
Phenyldibromoarsine	0.2	15.5	6
Phenyldichloroarsine	0.26	28.5	3
Ethyldichloroarsine	0.5	70	5
Methyldichloroarsine	0.56	85	4
Dibromoethyl sulfide	1.0	99	7

* Prentiss, *Chemicals in War*. McGraw-Hill, New York, 1937.

D. SYSTEMIC POISONS

1. HYDROGEN CYANIDE

Hydrocyanic acid or hydrogen cyanide, HCN (often called prussic acid), is a colorless gas with a penetrating odor resembling that of bitter almonds. It is highly toxic, acting directly on the nervous system. It can be absorbed through the skin so that masks are protective only for a short time.

Liquid hydrocyanic acid, known to the fumigation trade as liquid gas, or liquid cyanide, is a colorless fluid. It is exceedingly volatile in warm dry air, for it has a boiling point of 26° C. It melts at −15° C. It is lighter than water, having a specific gravity of 0.699. Large concentrations of the gas in air provide an inflammable mixture so that care must be taken to avoid igniting them. It is lighter than air, its vapor density being 0.95.

Liquid hydrogen cyanide was used by the French in World War I under the name Forestite and in combination with arsenious chloride under the name Manganite. Hydrogen cyanide is unlikely to be used extensively as a war gas because of its high vapor pressure and because it is lighter than air.

Hydrogen cyanide acts by stopping the oxidation of protoplasm in the

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[39] Hanzlik and Tarr, *J. Pharmacol.*, 221 (1919).

[40] Flury, *Z. ges. exptl. Med.*, **13**, 567 (1921).

tissue cells. At high concentrations, the symptoms appear rapidly, namely, giddiness, headache, unconsciousness and convulsions with cessation of respiration due to paralysis of the respiratory center in the brain. With weaker concentrations there may be the following symptoms: Irritation of the throat, palpitation, difficulty in breathing, watering of the eyes, salivation, headache, weakness of the arms and legs, giddiness—followed by collapse and convulsions. It is not a respiratory irritant.

The following table shows the effects produced by different concentrations of hydrocyanic acid vapor.

2. CYANOGEN CHLORIDE

Cyanogen chloride, CNCl, is a colorless, highly volatile liquid. It boils at 12.5° C.; solidifies at −6.5° C.; has a specific gravity of 1.2 and a vapor density of 2.1. One volume of water will dissolve 25 volumes of cyanogen chloride at 20° C. It is soluble in organic solvents like ether and alcohol but decomposes rather readily in alcohol. Cyanogen chloride polymerizes into cyanuryl chloride $(CNCl)_3$ which is physiologically inactive. During World War I it was used alone and in combination with arsenious chloride.

TABLE 9

EFFECTS OF HYDROCYANIC ACID VAPOR*†

PARTS PER VOLUME APPROX.	MG. PER LITER APPROX.	EFFECTS
1 in 50,000	0.025	Slight symptoms after several hours
1 in 10,000	0.12	Very dangerous within one hour
1 in 500	2.5	Fatal

* *Dept. Sci. Ind. Research Brit.*, Leaflet No. 2 (1938).

† *Analyst*, **63**, 658 (1938).

Cyanogen chloride, in addition to being a systemic poison, is a lachrymator and is used as a warning agent in commercial fumigation with hydrogen cyanide. Concentrations of the order of 0.0025 mg. per liter of air induce copious watering of the eyes. A concentration of 0.5 mg. per liter is intolerable and exposure to a concentration of 0.4 mg. per liter for 10 minutes is probably a lethal exposure.

3. CYANOGEN BROMIDE

Cyanogen bromide, CNBr, is a solid which forms transparent crystals melting at 52° C. It has a sharp penetrating odor, boils at about 61° C., has a specific gravity of 1.9 and a vapor density of 3.6. It is not readily soluble in water but dissolves more readily in alcohol and the usual organic solvents. In World War I, it was used in mixtures with bromoacetone dissolved in benzene. This mixture was known as Campiellite by the French.

It is a fairly strong lachrymator and irritant as well as systemic poison; 0.006 mg. per liter will affect the conjunctiva and the mucous membranes of the respiratory tract. The limit of intolerance is 0.085 mg. per liter, although some authorities give a lower concentration as the intolerable limit. It can cause death.

4. ARSINE

Arsine, AsH_3, is a colorless gas with an extremely offensive odor resembling that of garlic. It liquefies at −55° C. and solidifies at −119° C. It is 2.7 times as heavy as air. It is somewhat soluble in water but is insoluble in ether and alcohol. It decomposes on heating and is inflammable.

Arsine has not been used as a war gas because of its physical properties but many of its organic derivatives, as noted in previous sections, have been employed as war gases. It may be possible, however, that it acts as the decomposition product of some of these compounds.

Arsine is a cell, nerve and blood poison. There is generally some delay, sometimes a day or so before the onset of symptoms of acute poisoning. These are at first usually indefinite. There is a general feeling of malaise, difficulty in breathing, severe headache, giddiness, fainting fits, nausea, vomiting and gastrointestinal disturbances.[41, 42] In more severe cases the vomiting may be more pronounced, the mucous membranes may have a bluish discoloration, and the urine is dark or blood-stained. After a day or two, there is severe anemia and jaundice characteristic of chronic arsine poisoning.

A concentration of 500 parts of arsine per million of air is lethal for men after exposure of a few minutes. A concentration of 250 parts per million, equivalent to 0.75 mg. per liter is dangerous to life for exposure of 30 minutes. Concentrations of 6.25–15.5 parts per million, that is 0.02–0.05 mg. per liter are dangerous after exposure for 30 to 60 minutes. The maximum concentration tolerated for several hours without serious symptoms is 3.1 parts per million.[43] Sayers[42] gives a concentration of 10 parts per million as the concentration that can be tolerated for several hours without serious symptoms. There are no recorded figures as to the limits of concentration that may be regarded as harmless for continuous daily exposure, but there is evidence that repeated exposures to very low concentrations may have cumulative effects resulting in severe poisoning.[41]

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[41] *Dept. Sci. Ind. Research Brit.*, Leaflet No. 9 (1940) *Analyst*, **65**, 354 (1940).

[42] Sayers, *International Critical Tables.* (Vol. II) New York, 1927.

[43] Flury and Zernik, *Schaedliche Gase.* Springer, Berlin, 1931.

5. HYDROGEN SULFIDE

Hydrogen sulfide, H_2S, is a colorless, inflammable gas with an offensive odor like that of rotten eggs. It boils at −62° C., melts at −83° C., and is 1.19 times as dense as air. It is soluble in water, alcohol and carbon disulfide.

Hydrogen sulfide is unlikely to be used as a war gas. However, it may occur as a decomposition product of some of the chemical agents and explosives, and may possibly be used in mixtures of chemical agents.

In concentrations of 1 in 1000 by volume or higher, hydrogen sulfide will cause immediate unconsciousness, and will result in death unless artificial respiration is immediately applied. In such concentrations it is nearly as toxic as hydrogen cyanide and may act with equal rapidity by paralyzing the respiratory center of the brain. Hydrogen sulfide, however, differs from hydrogen cyanide as a poison, in that it is not absorbed through the skin. In general, its action depends upon its concentration and even a concentration of 0.005 per cent will cause poisoning. The effects of hydrogen sulfide for weaker concentrations, are summarized in Table 10.

Table 10

Effects of Hydrogen Sulfide*

CONCENTRATION IN AIR		EFFECTS
Parts by volume	Mg. per liter	
1 in 2000	0.76	Very dangerous if inhaled for 15 to 30 minutes. Causes severe irritation of the eyes and respiratory tract with risk of pneumonia or serious injury to the lungs, which may readily prove fatal.
1 in 5000	0.304	Dangerous if inhaled for one hour. Causes severe irritation of the eyes and respiratory tract. Eyes are affected after 6 to 8 minutes.
1 in 10,000	0.152	Symptoms of local irritation of eyes and respiratory tract after *one* hour's exposure.

* *Dept. Sci. Ind. Research Brit.*, Leaflet No. 1 (1937); *Analyst*, **62**, 607 (1937).

While hydrogen sulfide may be detected by smell, the sense of smell is lost in 2 to 15 minutes exposure to 0.010 to 0.015 per cent of this gas.

6. CARBON MONOXIDE

Carbon monoxide, CO, is a colorless and odorless gas. It is combustible and is lighter than air, having a specific gravity of 0.967. It used to be termed "white damp" by miners but that is an inappropriate term. Air containing 12.5 to 74 per cent of carbon monoxide will explode if ignited.[44, 45] Therefore 12.5 per cent and 74 per cent are known as the

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[44] Coward and Jones, *U. S. Bur. Mines*, Bull. No. 279 (1928).

[45] Jones, *U. S. Bur. Mines, Tech. Papers* **450** (1929).

upper and lower explosive limits. The gas liquefies at −190° C. and solidifies at −207° C. Carbon monoxide is unlikely to be used as a war gas because of its extreme lightness but it may be formed as a decomposition product of explosives and some chemical agents. Iron carbonyl, $Fe(CO)_5$, may be used to produce carbon monoxide by decomposition.

Carbon monoxide in excess of 0.01 per cent, if breathed for a sufficiently long time, will produce symptoms of poisoning. As little as 0.02 per cent will produce slight symptoms in several hours. Four parts in 10,000, which is equivalent to 0.04 per cent, will produce headache and discomfort within 2 to 3 hours. With moderate exercise 0.12 per cent will produce slight palpitation of the heart in 30 minutes, a tendency to stagger in 1½ hours, and confusion of mind, headache, and nausea in 2 hours. A concentration of 0.20 to 0.25 per cent will usually produce unconsciousness in about 30 minutes. Its effect in high concentrations may be so sudden that a man has little or no warning before he collapses.[46] These symptoms are summarized as given in Table 11.

TABLE 11

CARBON MONOXIDE POISONING*†

EFFECT	CO PER CENT
Allowable for an exposure of several hours	0.01
Can be inhaled for one hour without appreciable effect	0.04–0.05
Causing a just appreciable effect after one hour's exposure	0.06–0.07
Causing unpleasant but not dangerous symptoms after one hour's exposure	0.1 –0.12
Dangerous for exposure of one hour	0.15–0.20
Fatal in exposure of less than one hour	0.4 and above

* Frederick, *Analyst*, **56**, 561 (1931).

† Henderson and Haggard, *Noxious Gases*. Chemical Catalog Co., New York, 1927.

Carbon monoxide is really a chemical asphyxiant because it produces its harmful effect by combining with the hemoglobin of the red blood cells to form a relatively stable compound, carbon monoxide hemoglobin, usually abbreviated HbCO, thereby depriving the body of oxygen by preventing this combined hemoglobin from taking up oxygen to form oxyhemoglobin, HbO_2. The affinity of carbon monoxide for hemoglobin is about 300 times that of oxygen. Hence, if only a small amount of carbon monoxide is present in the air taken into the lungs, the carbon monoxide will be absorbed in preference to the oxygen by the blood. Carbon monoxide asphyxia, and probably other types of asphyxia, produce degenerative changes in nerve cells and throughout the entire brain.[47]

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[46] Forbes and Grove, *U. S. Bur. Mines, Miners' Circ.*, **33** (1938).

[47] Yant, Chornyak, Schrenk, Patty and Sayers, *U. S. Pub. Health Service*, Bull. No. 211 (1934).

E. SCREENING SMOKES

A screening smoke is a cloud of minute particles of solid or liquid suspended in the gaseous medium, air. It is used to destroy visibility entirely or to create a haze which lowers visibility considerably. A screening smoke fulfills its object by the scattering of rays of light rather than by actual obstruction of light. The more numerous the particles, the more effective the screening power, provided the particles are large enough to reflect light. A good smoke material is one which will give a great number of highly dispersed particles down to a minimum size.

A white smoke is more effective than a black smoke because it reflects more light and the diffusion of light is the function of a good smoke. A smoke consisting of deliquescent particles will also make for better obscuring power because the particles too small to reflect when dry, grow large enough in a humid atmosphere to do so.

Smokes are rated according to total obscuring power, usually abbreviated T. O. P. T. O. P. is the number of cubic feet of unit density which can be obtained from one pound of the smoke material. Unit density is sufficient density of a smoke to obscure the light of a 25 watt lamp at a distance of 1 foot.

Classification of Smokes

There are five principal types of smoke materials used:

(1) Colloidal carbon.—

Crude oil is the principal material used for the formation of colloidal carbon smokes. It forms the smoke by being incompletely burned. It is a black smoke composed largely of free carbon and tarry matter.

(2) Phosphorus.—

White phosphorus forms a smoke by burning to form particles of phosphorus pentoxide, P_2O_5, which is a white, extremely deliquescent substance. The phosphorus pentoxide is hydrolyzed to form droplets of phosphoric acid, H_3PO_4, by the water vapor in the air and thus the smoke is formed of particles of P_2O_5 and droplets of H_3PO_4.

(3) Sulfuric acid and oleum.—

Sulfuric acid, oleum, and chlorosulfonic acid, $HOSO_2Cl$, when heated, produce dense white fumes of the respective acids and acid anhydrides. A combination of SO_3, sulfur trioxide, and $HOSO_2Cl$, chlorosulfonic acid, is known by the American symbol FS.

(4) Hydrochloric acid fumes.—

Certain chlorides such as tin tetrachloride, $SnCl_4$, titanium tetrachloride, $TiCl_4$ and silicon tetrachloride, $SiCl_4$ are readily hydrolyzed with the formation of the respective hydroxides, $Sn(OH)_4$, $Ti(OH)_4$, and $Si(OH)_4$ and hydrochloric acid. The smoke produced is formed from the fumes of hydrochloric acid and the particles of hydrated tin, titanium and silicon oxides. The principal agent of this group is titanium tetrachloride, which is known by the American symbol FM.

(5) Zinc chloride.—

The fumes are produced by the combustion of a halogenated hydrocarbon with zinc and zinc oxide with the formation of zinc chloride, $ZnCl_2$, a white, highly deliquescent substance undergoing hydrolysis with the formation of hydrochloric acid and zinc hydroxide.

The principal American mixture, termed HC, consists of zinc, zinc oxide and hexachloroethane, which react according to the equation:

$$3Zn + C_2Cl_6 \rightarrow 3ZnCl_2 + 2C$$

A similar mixture, also termed HC, consists of $Zn + C_2Cl_6 + NH_4ClO_4 + NH_4Cl + CaCO_3$. Other mixtures are the BM mixture: $Zn + CCl_4 + NaClO_3 + NH_4Cl + MgCO_3$ and the Berger mixture: $Zn + CCl_4 + ZnO +$ kieselguhr.

Since the primary object of a smoke is to make itself visible and other objects invisible, its presence is sufficient for detection. In order to determine the character of a particular smoke, it may be sampled and analyzed by the methods detailed in Jacobs, *Analytical Chemistry of Industrial Poisons, Hazards and Solvents.*

F. INCENDIARIES

The term incendiaries includes all materials which are used in warfare to produce fire either for destruction or for use as a means of combat.

The incendiaries may be placed into seven principal groups:

(1) White phosphorus
(2) Thermites
(3) Other oxidizing agents
(4) Inflammable materials, like petroleum, gasoline etc.
(5) Solid oils, partially saponified oils
(6) Spontaneously inflammable liquids
(7) The active metals, sodium, potassium and magnesium.

White phosphorus does not have much value as an incendiary because it will not ignite less readily combustible materials, such as dense wood; it needs oxygen in order to burn, and it forms a fire-proof coat of phosphoric acid. It readily ignites easily combustible materials.

Thermites are mixtures of iron oxides and aluminium. They need a high temperature to ignite, (about 1800° C.) but once ignited, they need no additional oxygen:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$$
$$3Fe_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Fe$$

Water glass and sulfur are used as binders. Daisite is a sulfur-bound thermite. Burning magnesium ribbon is often used as the igniting agent.

The thermites are valuable incendiaries because they can produce a very high temperature quickly in a localized spot.

Inflammable materials and solid oils serve as incendiaries because once they begin to burn, they produce a very hot flame and thus will cause surrounding objects to burn. They may be ignited by gunpowder.

Zinc ethyl, phosphine, silicon hydride and phosphorus in carbon disulfide are materials which ignite spontaneously. As a chemical agent, only the last mentioned is of practical value.

Oils on water may be ignited by means of sodium or potassium. However, sodium and potassium have practically no action on dry materials and can be stored under kerosene.

Substances like petroleum, gasoline, fuel oil, kerosene, pitch etc. generate from 8,400 to 11,500 gram calories of heat, which is far greater than that produced by other incendiaries. For instance, phosphorus and magnesium produce about 6,000 gram calories, sodium generates about 2,200 and thermite only 800 gram calories. However, most inflammable substances have disadvantages which restrict their use as incendiaries. Thus, the incendiary action of gasoline, for example, is upward and it is too light to use effectively in small bombs.

The most effective incendiary agent used in air raids is the magnesium bomb, often called the Elektron* bomb or kilo because it weighs 1 kilogram, that is, 2.2 pounds. This bomb has a shell or casing of a magnesium alloy and a core of thermite priming composition. The principal advantage of this incendiary is that the entire bomb is combustible except for the tail and striker mechanism. It also burns for a longer period than other incendiaries.

When the bomb strikes a hard surface, the impact sets off a fuse which ignites the thermite core. This burns fiercely for about 1 minute at about 3,000° C. and melts and ignites the magnesium alloy casing. After some spluttering during this minute, whereby burning metal may be thrown for as much as 30 feet, the bomb collapses into a pool of molten, burning metal which continues to burn for 10 to 15 minutes with intense heat. This burning, molten magnesium is the principal danger for it will set fire to anything inflammable within a radius of several feet.

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* German trade mark of a magnesium alloy.

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III. EFFECT OF WAR GASES ON MATERIALS, WATER AND FOOD; SAMPLING

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I. Materials

The chemicals used in chemical warfare are nearly all liquid or solid at ordinary temperatures, as has been explained in Chapters I and II, but they are sufficiently volatile to permit an appreciable proportion of each existing as a gas. Volatility affects penetration of foods and other materials and subsequent decontamination by airing. In general, the more volatile the chemical agent, the more rapidly it will diffuse into the air spaces adjacent to the material or into the air spaces in granular materials and foods, and the more rapidly it will subsequently diffuse out again and be removed by aeration. However, some of the vapor of even the most volatile of the war agents will probably be absorbed or adsorbed by the outer layers of the material, if such absorption or adsorption is possible. The more volatile liquids, that is, the non-persistent agents, will vaporize rapidly, many of them completely if liberated from a bomb, and most of the vapor will often be carried away by air currents before serious contamination can occur. The less volatile liquids, that is the persistent agents, will continue to vaporize for a long period, the length of time depending on local conditions, such as temperature, protection from winds, drafts and rain. The vapors of persistent agents will be more readily absorbed or adsorbed from a given concentration in air than those from the non-persistent or more volatile liquids, but again they will be retained mainly in the outer layers of the material.

The most serious contamination arises from contact of the material or food with the chemical warfare agent in the form of splashes of liquid or of spray. Such contact will, generally, be limited to the persistent agents, since the others will be mostly vaporized at the moment of liberation.

However, heavy contamination by the liquid form of any war gas is difficult to remove by aeration alone. This applies even to low-boiling liquids such as hydrogen cyanide, whose boiling point is 26° C.

Liquid splashes of chemical agents, which constitute the principal source of pollution, have different effects according to the nature of the surface on which they fall. If they fall on an absorbent surface, they will seep into it and take longer to evaporate under normal conditions. Furthermore, they will be more difficult to remove and to decontaminate by chemical means.

War gases in the liquid state will penetrate into earth; consequently pools of an agent like liquid mustard gas or even large visible splashes of this substance are rarely found on the ground. The liquid agents are absorbed by wood, by textiles, by foods etc., if not protected by impervious coverings. Since many of the war gases are of an oily nature, particularly the vesicants, they are readily absorbed by other oils such as lubricating oil on machinery, food oils and fats and the oils of the skin, by tar products such as roofing materials, asphalt road surfaces and the like. Mustard gas vapor has a deleterious effect on lubricating oil. Porous materials and articles like concrete, brick, mortar, stone, unglazed tile, unglazed earthenware, etc. will also absorb liquid war gases. Acid forming agents are very damaging to paint work.

The depth of penetration and the degree of absorption will depend, as one can readily see, on the character of the particular surface involved and the length of time the war agent is in contact. Danger and damage may be reduced and, at times, prevented if action can be taken promptly to decontaminate a polluted material, area, or object.

The principle effects of chemical agents on materials are corrosion and rotting.

II. Metals

Many of the war gases hydrolyze with the formation of an acid like hydrochloric acid or sulfuric acid, (See Table 23, page 140) consequently these chemical agents will have a corrosive effect on metals. Among the more important gases which have a vigorous corrosive effect on metals, particularly if wet, are chlorine, phosgene, xylyl bromide, diphenylchloroarsine, bromobenzyl cyanide, sulfur trioxide smoke solution, and the tin and titanium tetrachlorides. Benzyl chloride vigorously attacks iron, tin and copper. Cyanogen bromide has a strong corrosive action on most metals, even lead and brass.

Chloropicrin, mustard gas, diphenylaminechloroarsine, and Lewisite have only slight action, while chloroacetophenone has a tarnishing effect on steel.

III. Textiles and Leather

Textiles, in general, will absorb liquid chemical agents readily. Most animal fibers, like wool and silk, absorb the vapor of war gases more readily and in greater quantity than vegetable fibers. However, the strength of vegetable fibers like cotton is noticeably lowered by this absorption, while that of the animal threads is practically unchanged. If not decontaminated, the material, particularly cotton goods, canvas, rope and hemp, will rot. Cotton goods, canvas and the like can be decontaminated as described on page 155, but if rope is heavily contaminated with mustard gas, it should be destroyed because the mustard gas will remain in the core of the rope, from which it cannot easily be removed, and will rot it. Some agents, like bromoacetone, discolor textiles.

Leather, unless specially treated, absorbs mustard gas very quickly and is difficult to decontaminate.

Rubber goods absorb the vesicants slowly; hence they are not impervious to penetration by these gases. Phosgene rapidly attacks rubber goods. Acid forming agents like chlorine, phosgene and the screening smokes, FM and FS rot fabric, rubber and leather, particularly if the exposure is prolonged.

IV. Water

Very large volumes of water such as are impounded in large reservoirs will be very difficult to contaminate to any significant extent. Little danger is to be feared from such water sources, particularly if the customary purification processes of coagulation, sedimentation and filtration are carried out.

Smaller volumes of water, such as are held in small reservoirs of the order of 3,000,000 gallons, in pools or in tanks, should be analyzed for the presence of contaminants, particularly arsenic, before being used for drinking purposes. Still smaller volumes of water such as in cisterns, wells, small tanks, etc. should merely be discarded or not used, except in the case of some great emergency, when these stores should be analyzed also.

Mustard gas is only slightly soluble in water and is only slowly hydrolyzed by cold water. Hence, if mustard gas falls on water, it will sink to the bottom, since it is heavier than water; there it can remain active for some time. The hydrolytic products are relatively innocuous, so that such water can be rendered fit to drink by filtration, chlorination, etc. Lewisite, on the other hand, is readily hydrolyzed by water with the formation of chlorovinylarsenious oxide, a toxic substance, which is sparingly soluble in water. Such waters may, however, contain poisonous amounts of arsenic. It is best to test any water suspected of contamination with arsenical war gases before use.

IV. Foods

The extent of damage to foods contaminated by chemical warfare agents will depend on the chemical and physical properties of the war gases used and the food itself, as well as on the degree of exposure of the food to the chemical warfare agents. Foods and war gases may be put into 2 main groups by consideration of these properties and the probable extent and nature of contamination can be forecast. Generally speaking, all foods contaminated by arsenicals and white phosphorus, and fatty foods contaminated by non-arsenical vesicants like mustard gas, will be poisonous despite any decontamination treatment, while foods contaminated with other agents may be considered relatively non-poisonous, especially after adequate salvaging operations. However, it is to be noted that food seriously contaminated with chloropicrin cannot be salvaged by cooking since this substance is not hydrolyzed by water.

Foods absorb chemical warfare agents by solution in the water or fat which they contain or by adsorption on their solid surfaces. Either process may be followed by a reaction which involves some degree of decomposition of the chemical agent. The principal chemical reaction is hydrolysis, or splitting of the chemical agent by the action of water. By this means the absorbed substance will generally lose its poisonous properties, and so will be rendered comparatively innocuous. Hydrolysis of chemical warfare agents does not always result in the formation of innocuous substances. Lewisite and other arsenical chemicals are still poisonous after they have been hydrolyzed, although at times their vesicant properties will have been destroyed. The hydrolytic product of Lewisite is a vesicant solid. The hydrolysis of chemical agents is a much slower process than their solution in water, hence foods containing considerable water or liquids which have been contaminated may remain harmful for a long period, despite gradual hydrolysis, depending on the initial degree of contamination. Many of the decomposition products of the war gases are unpleasant and may render the food unpalatable although not actually deleterious.

Solution of chemical agents in fats is seldom followed by any chemical reaction comparable to that of hydrolysis. Hence the surface of a fatty food, once it is contaminated, is usually rendered permanently unfit for human consumption.

The chemical warfare agents most likely to be used are, in accordance with the previous discussion, phosgene, persistent tear gases like bromobenzyl cyanide, non-arsenical vesicants, arsenical smokes, and arsenical vesicants. The effect which these war gases have on foods is discussed in the following sections.

1. PHOSGENE

Prolonged exposure to a relatively high concentration of a non-persistent war gas of the phosgene type, such as might easily occur in low, confined spaces, may cause slight deterioration, but such exposure is more likely to affect palatability than to render the food entirely unwholesome as an article of diet. In Table 12 the effects of high concentrations of phosgene on foods is summarized. Foods contaminated with phosgene are not likely to be dangerous but any possibility of danger may be largely removed by aeration and ventilation of the food for 48 hours and, where practicable, cooking. More or less hydrochloric acid may be formed and this will impart a sour taste. Bleached portions of the food should be cut away; in the case of cheese and fats, these parts may be used in cooking. The baking properties of undiluted contaminated flour will be damaged but, after aeration, the flour may be blended with five times as much fresh flour and then used.

TABLE 12

EFFECTS OF HIGH CONCENTRATION OF PHOSGENE VAPOR ON FOODS*

FOOD	EFFECT	SALVAGE OPERATION
Flour	Becomes sour and slightly unpalatable	48 hours airing. Can then be blended with 5 parts of undamaged flour and will bake normally
Bread	Outer layers may become unpalatable	Cut away outer layers and air the remainder
Cereals	Negligible	48 hours airing
Meat and fish	May become slightly discolored on the surface	Condition improved by airing and cooking
Milk	May slightly affect taste	Bring to boil
Eggs	None	
Cheese, butter, margarine and fats	May bleach slightly on surface	If bleached, cut away affected part, which may be used for cooking. Remainder is edible
Fresh fruits	Almost none	Air and peel off skin or outer layer
Dried fruits	Slight loss of palatability	Air and cook
Fresh vegetables	Green vegetables may be slightly bleached	Air and cook
Tea and coffee	May become bitter and unpalatable	None is effective, but such material might be used for blending

* Ministry of Food (Brit.) *Foods and its Protection against Poison Gas* (1941).

2. PERSISTENT TEAR GASES

Persistent lachrymators will, in all probability, seldom be used for attacking civilian centers because the damage they might cause would not be commensurate with the effort expended. Foods contaminated either by the liquid or vapor of these poison gases will be rendered highly unpalatable. Ventilation and aeration are the only treatments likely to be of any value in attempts to salvage such contaminated foods but if the food is badly contaminated such treatment will be relatively useless. In such instances the food must be discarded.

3. NON-ARSENICAL VESICANTS

The principal agent in this group is, of course, mustard gas. The vapors of mustard gas and other blister agents, such as methyl sulfate, which do not contain arsenic may be harmful to foods if the time of exposure is long and the concentration of the vapor is high. Slight contamination will affect the palatability of exposed foods but, with the exception of fatty foods, they should be edible after aeration and ventilation for 48 hours followed by cooking. Fatty foods must be regarded with suspicion after exposure to a non-arsenical vesicant for they are likely to absorb the vapor.

TABLE 13

EFFECT OF EXPOSURE OF UNPROTECTED FOODS TO LOW CONCENTRATIONS OF MUSTARD GAS*

FOOD	EFFECT	DANGEROUS	SALVAGE OPERATION
Bread, flour, cereals, lean meats, white fish, eggs, fresh and dried fruits, vegetables, tea, coffee, sugar condiments	In most cases no ill effect is noticeable after treatment. In others there may be a slight loss of palatability	No	Aeration is the general treatment. With some foods, such as lean meat, the surface layers can be cut away
Milk, cream, butter, margarine, fats, oils, fatty meats, fatty fish, cheese	Rapidly absorb gas and may become unpalatable	Probably	None effective

* Ministry of Food (Brit.) *Food and its Protection against Poison Gas* (1941).

Foods which come in contact with liquid non-arsenical vesicants must be regarded with deep suspicion; in particular fatty foodstuffs such as milk, cream, butter, margarine, cheese, lard, bacon, fatty meats, salmon, herrings, kippers, salad oils, chicken grease etc. will almost certainly be highly dangerous. Such foods must be discarded and cannot be salvaged. The effect of exposure of unprotected foods to low concentrations of mustard gas is summarized in Table 13.

It is interesting to note some of the results obtained by experimental impregnation of foods with mustard gas.[1]

Foods contaminated or impregnated with mustard gas lost their poisonous qualities as the temperature increased. Bread, bacon, and other relatively dry foods treated with 0.1 ml. of mustard gas are poisonous for

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[1] Hasskò, *Z. Untersuch. Lebensm.*, **79**, 296 (1940) *Analyst*, **65**, 427 (1940).

at least 20 days at 12° C., and for only 6 to 8 days at 20° C. Flour only moderately impregnated may remain poisonous for more than a month at 16° C. Sausages in Cellophane skins withstand the action of the gas for many days, but sausages with skins made from intestines absorb the gas rapidly and lose it only slowly in air. Milk treated with 0.01 ml. of the gas is poisonous after being boiled several times, whereas water treated with 2 ml. of the gas per 10 ml. of water is drinkable after several filtrations through activated carbon. Dry foods show little evidence of mustard gas contamination but with moist foods, brown spots or surface changes are soon visible, cucumber and marrow being particularly sensitive. Green peppers, green beans, peas, pears, gooseberries, apples, lemons, and oranges show visible changes only after 24 hours, beets and radishes only after 3 days. Some types of grapes turn brown. Meat obtained from animals which had been given oral doses of mustard gas may not be poisonous.

4. NON-PERSISTENT ARSENICAL AGENTS

The arsenical non-persistent gases such as diphenylchloroarsine, diphenylaminechloroarsine, and diphenylcyanoarsine, are released in the form of clouds of fine particles which are readily dispelled. It is not likely that such a cloud would significantly affect protected foods with which it came in contact. Airing would be the appropriate treatment in such an instance but any unprotected food would risk being contaminated. Affected food must be examined by an expert before being released for consumption. A high concentration of any arsenical gas in an enclosed space might contaminate foodstuffs with sufficient arsenic to render the food dangerous for consumption. If there is the slightest suspicion that an arsenical gas has contaminated a food, report it to the proper authorities.

5. ARSENICAL VESICANTS

The most serious contamination of this nature that is likely to occur is that of contact with liquid Lewisite but the poisonous agents like methyl, ethyl and phenyldichloroarsine, should not be overlooked. While some portion of these arsenical compounds may be removed unchanged by aeration and ventilation, a large proportion will be held firmly bound in solution in the fats or by hydrolysis by the water present in the food. If there is the slightest suspicion that food has been in contact with a solid, liquid or vapor containing arsenic, the food must not be eaten until it has been declared harmless as the result of analysis by an expert of a governmental agency.

6. SCREENING SMOKES

Most screening smokes have a deleterious action on foods. All smokes give a disagreeable odor to the food they impinge upon and may render them unpalatable. The liquid from smokes like titanium and tin tetrachloride may make the food harmful. The liquid from sulfur trioxide-chlorosulfonic acid smoke renders both food and water unfit for use. While the smoke from white phosphorus merely gives food a disagreeable odor and may make it unpalatable, contamination with the solid in quantity is distinctly poisonous and the food cannot be salvaged.

VI. Growing Crops[2]

Growing crops contaminated by liquid mustard or Lewisite will show scorching and bleaching. Plants thus affected by mustard gas should eventually recover and the fresh growth will be entirely wholesome. The time for recovery will depend on the weather, but may average about a week. Lewisite and other arsenicals will cause much more protracted damage. Sampling will be extremely difficult, and great caution would have to be exercised in drawing conclusions from the examination of samples.

VII. Livestock

Animals are often as readily incapacitated by exposure to poison gas in any form as human beings. They may also be harmed by grazing pasture or eating fodder or feed which was polluted by persistent chemical agents, although some animals instinctively refuse to eat such tainted feed. It will probably be necessary to slaughter livestock showing symptoms of gas poisoning as a result of the inhalation of war gases or consumption of foodstuffs contaminated by these agents. The carcasses of such animals may not necessarily be unfit for human consumption. However in doubtful cases, samples should be taken and the food should be analyzed.

VIII. Sampling

The problem of adequate sampling for the detection, identification and determination of the war gases is a complex one, and is somewhat different from that of ordinary sampling. The fundamental purpose of sampling, and for that matter of field testing, is to enable the chemist, war gas inspector, health officer, gas identification officer or other official sampler as rapidly as possible (1) to detect the presence of a chemical warfare agent; (2) to recognize its physiological classification; (3) to determine, if possible, the concentration of the agent and from this the potential hazard; (4) to ascertain the extent of the polluted area, and therefore the dangerous areas; (5) from this data aid the proper authorities in selecting the best procedure for the decontamination of materials and the salvaging of foods.

Obviously the official sampler must be adequately clothed with anti-gas

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[2] Page, *J. Roy. Sanit. Inst.*, **61**, 155 (1941).

clothing, which, being bulky and relatively unwieldy, will hamper his movements somewhat. This type of clothing and the procedures for putting on and taking off such clothing is described in a number of government publications.[3,4,5,6] Some practice in sampling with these outfits in unpolluted areas is necessary in order to gain experience.

The necessary anti-gas clothing will consist of a light anti-gas jacket, light anti-gas trousers (an anti-gas coverall or, permeable impregnated clothing, if available, is satisfactory) an anti-gas helmet or hood, rubber boots or impregnated shoes, anti-gas gloves and a gas mask. In addition, the inspector will require certain special equipment for the taking of samples and for the performance of field tests.

It is important that first aid should be available for all persons coming into contact with poison gas through sampling, analytical or decontamination work.

1. TYPE OF SAMPLE

The type of sample to be taken may be placed into two principal categories. First, samples of contaminated air may be required. In such instances it may be preferable to perform tests directly in the field. Second, samples of polluted materials and food may have to be taken. In the latter case, the pollution may be due to (1) actual contact contamination with the liquid poison gas, with the spray from chemical agents, or with the dust of arsenical smokes or screening smokes, and (2) exposure only to the vapor of these agents. In the case of food products, type (1) pollution is of much greater moment than type (2) pollution.

2. AIR SAMPLING

There are two basic methods of sampling. The first method is to obtain a definite volume of air within a gas collector, at a known pressure and temperature, in a manner entirely analogous to the ordinary sampling of gases.[7] This sample is then taken to the laboratory to be analyzed or is analyzed in the field. The second basic method is to pass a known volume of air or gas through an absorbing medium or solution or equivalent means. The noxious material or contaminant is thus absorbed or adsorbed and the absorbing or adsorbing medium or agent is subsequently subjected to

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[3] A. R. P. Training Manual No. 1 *Basic Training in Air Raid Precautions*. Brit. Library Information, New York, (1940).

[4] A. R. P. Handbook No. 1, *Personal Protection Against Gas*, Brit. Library Information New York, (1939).

[5] United States Office of Civilian Defense, *Protection Against Gas*, Washington, D. C. 1941.

[6] United States Office of Civilian Defense, *Decontamination Squads*, Washington, D. C. 1941.

[7] Yant and Berger, *U. S. Bur. Mines, Miners' Circ.* **34** (1936).

analysis either in the field or preferably in the laboratory. Where the gross components of a gas or of air are to be estimated, the first basic sampling method may be used; where a small or minute amount of a contaminant is to be estimated, as will be the case in sampling air for war gases, the second basic sampling method is to be preferred.

Where a definite volume of gas is required or desired as the sample to be analyzed, there are two possible types of sample that may be taken. These are known as "instantaneous" (also known as "grab", "spot", and "snap") samples and "continuous" samples. Instantaneous samples are those taken at a particular time and place within an interval of a few seconds to a minute or two and represent the composition of the air or gas at that time and location. They are most often taken with evacuated bottles or gas collectors, although they may be taken with liquid displacement devices.

Continuous samples are taken where a comparatively large volume of gas must be sampled or where the composition of the air being sampled is not uniform. In the former case, it is necessary to pass the air or gas through some absorbing agent in order to trap the contaminant to be estimated. In the latter instance, a sample taken continuously for a given period of time will give the average composition. It may be preferable, if the composition of the gas or air is not uniform, to take several grab samples at different times and locations rather than to take one continuous sample.

For air samples, the war gas inspector must have a kit comprising a small hand suction pump or a rubber bulb suction aspirator, absorption bubblers, absorbing solutions like water and dilute alkali, adsorbing materials like activated charcoal, silica gel, absorbent cotton, and miscellaneous material for recording his samples, sealing the samples, and shipping the samples to the laboratory. Adsorbents are better for sampling non-persistent gases. Absorbent cotton is better for particulate clouds like the toxic smoke. The reader is referred to Jacobs, *The Analytical Chemistry of Industrial Poisons*, *Hazards and Solvents* for descriptions of various devices used in the sampling and detection of industrial poisons in air. Some of these devices may be readily used for the sampling of war gases.

It may be best to use a simple but efficient bubbler through which to aspirate the air to be tested. This aspiration should be done slowly. As far as possible rubber connections should be avoided, and the use of small sintered glass diffusers will enable the air to be passed into and absorbed by a minimum volume of the reagents employed for the tests. The number of gases which undergo hydrolysis in water or dilute alkali, makes it possible to perform direct tests for the products of hydrolysis as described on page 81.

Sampling tubes for trapping vapors in general may be prepared as follows: Insert a plug of absorbent cotton into the tubes followed by about 0.2 gram of 7–18 mesh activated carbon granules. Finally put in a second plug of absorbent cotton, pressing the latter firmly into position.

3. SAMPLING OF MATERIALS

The sampling of materials for the detection of chemical warfare agents, resolves itself chiefly into the sampling of such materials as soil, leaves, rubble, etc. which have been sprayed by the gas during an attack. For sampling, other than that of air or food, the equipment of the war gas inspector should comprise, in addition to the protective clothing previously mentioned, a partitioned metal case, capable of being suspended from a regulation webbed belt, containing 4- or 8-ounce wide mouth, plastic material, screw-cap sample-bottles, numbered serially for identification; some wooden spatulas; a stainless steel forceps; absorbent cotton swabs; a bottle of sodium hypochlorite solution; filter paper; a flash light; a pencil and report forms. In addition, an auxiliary soldier's bag made of anti-gas material which can be attached to the webbed belt, should be used for holding metal cans into which the bottles containing the samples may be put. The lids of these tin cans should be taped with adhesive for better anti-gas protection. For food sampling, and for field tests still other equipment described below is needed. If bakelite or other plastic material screw-cap bottles are unavailable, ordinary metal screw cap bottles may be used, but the mouth of the bottle should first be covered with cellophane or greaseproof paper.

Procedure.—The war gas inspector and his assistant should go to the area or building or other place where the samples are to be taken and should place themselves upwind, if possible.

Open the sampling case, take out a sample bottle, forceps, spatula, the bottle of sodium hypochlorite solution, the cotton swabs, some filter paper and reclose the case. Unscrew the bakelite cap and give it to the assistant or place it in the auxiliary bag. Let the assistant hold the hypochlorite solution and swabs. Place the forceps, spatula, filter paper etc. in the bottle and, holding it in the left hand, slip an anti-gas glove over the rubber glove on the right hand. Walk to the contaminated area or to the place where the material is to be sampled. Select a portion of the latter where the surface material is loose enough to be dug out with the spatula and forceps. If the material is of an impervious or very solid nature, soak up any visible drops of contaminant by means of the filter paper held by the tweezers and place the filter paper in the sample bottle. Using the spatula and forceps, fill the bottle with grossly contaminated material, taking care not to contaminate the outside of the bottle. Discard the wooden spatula on the ground and walk back to the original position upwind. Decontaminate the forceps by dipping it into the hypochlorite solution and wiping it with the absorbent cotton swabs. Place these swabs in a tin can reserved for waste and destroy later. Slip off the outer anti-gas glove. Take the plastic material cap and screw it on the sample bottle firmly. Remove the adhesive tape and lid from one of the metal cans, and put the sample bottle into the can. Replace the lid and the adhesive tape and place the can back into the auxiliary bag. Record the sample number.

From this point, other samples can be taken by repetition of the above procedure. At the end of sampling, the war gas inspector must go through the regular cleansing and decontamination procedure.[8,9] Decontamination of the outside of the metal sampling kit, the metal cans holding the samples and forceps may now be done with solvents as explained in Chapter VII. The unused materials, the webbed belt, the auxiliary bag, etc. may generally be decontaminated by airing but if badly contaminated, the methods described in Chapter VII should be used.

4. SAMPLING OF FOODS[10,11]

The sampling of foods polluted by chemical warfare agents presents special problems. It will generally be best to obtain samples from the surface of foodstuffs, from the surface and the interior of packages and preferably also from packages on the exterior and the interior of a pile. It is highly important that sampling be done carefully and systematically. One of the difficulties to bear in mind is the danger of contaminating clean food by sampling equipment previously used for polluted food. Contamination by liquids or heavy vapors will generally be uneven, hence the sampler should seek the most heavily contaminated portions. Apart from the concentration of damage on the surfaces, which will be the most likely, there will be differences from package to package. Careful examination and testing in the field for local concentrations of persistent gas should be made if possible, in order to decide on the plan of sampling. Such a course of action will not be possible, however, if many small stores have to be dealt with. Where such a condition exists, it may be best to take away a large proportion of the food for salvage by aeration and ventilation without analysis. Some combining of samples will have to be done to reduce the number of specimens to be analyzed. Sampling of vegetables after decontamination by thorough washing is obviously especially difficult.

As explained previously, contamination by liquid poison gas, by poison

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[8] United States Office of Civilian Defense, *Protection Against Gas*. Washington, D. C. (1941).

[9] United States Office of Civilian Defense, *Decontamination Squads*. Washington, D. C. (1941).

[10] Page, *J. Roy. Sanit. Inst.* **61**, 155 (1941).

[11] Woods, *J. Roy. Sanit. Inst.* **61**, 160 (1941).

gas spray, by the arsenical smokes, diphenylaminechloroarsine, diphenylchloroarsine, diphenylcyanoarsine or white phosphorus screening smoke is more harmful than exposure to a war gas vapor.

Procedure.—The sampling officer should be properly clothed and equipped. In addition to the equipment previously mentioned in this chapter, he should have a stainless steel knife. Following the procedure detailed on page 55, samples should be taken by cutting thin slices from various suspected portions and placing them in a clean, dry sample bottle. Another sample should be taken in the same way and from similar places, but at a depth of one inch from the surface, and placed in another bottle. This second specimen serves as a control on the depth of pollution.

The knife must be cleaned between each cut by dipping into a vessel containing bleaching powder mixed with water to a cream, or the sodium hypochlorite solution mentioned before, wiping the blade clean and drying with a piece of cotton waste. This waste is dropped into another bottle containing bleaching powder cream which can later be buried or burned. In every case the sample should be not less than four ounces in weight. The samples should be delivered to the chemist by hand, if possible. The sample bottles, and the consignment of goods from which the specimens were taken, must both be similarly labelled, so that it is possible to trace the exact source of the samples, if necessary.

Unprotected fatty foods such as butter, oleomargarine, cheese, lard, hydrogenated fats, sausages, cooked meats and carcasses are all very susceptible to penetration by mustard gas or Lewisite, and should therefore receive special attention. Thus, no distinction should be made between vapor or other types of contamination.

Foods wrapped in greaseproof paper like butter, oleomargarine, cakes, sausages, etc., are not so susceptible to contamination by spray as noted on page 161 but one or more unopened packages should be sent for analysis in suspected cases of liquid contamination. Aeration alone may suffice to salvage foods contaminated by vapors alone.

When liquid war gas or arsenical contamination is suspected in sacked goods like sugar or flour, samples from the affected portions should be taken for analysis. If it can be shown that only vapor pollution has taken place, the sacks may be reconditioned by aeration and ventilation.

Foods in cardboard cartons, paper bags, and jars with so-called parchment covers which may have been splashed with liquid, should be sampled for analysis by taking unopened specimens. Even if only vapor contamination has taken place, it would be advisable to take samples, since, as Table 26 shows, these coverings provide little protection. If goods packed in containers are stored in their packing cases or in drawers, very little damage even from liquid contamination need be feared.

Milk in open vessels should be destroyed without analysis, and even milk in bottles covered with cardboard disks should be discarded if splashed with liquid chemical agents.

Splashed vegetables should be destroyed. Vegetables contaminated by exposure to the vapor only may possibly be reconditioned by washing and aeration.

Eggs polluted by liquid contamination should be destroyed. If they are exposed only to vapor contamination, about a half dozen should be submitted for a chemical analysis.

Oily fish should be destroyed following contamination by liquid and spray of war gases but bulk lots should be sampled for chemical analysis. Fish polluted by war gas vapors may at times be rendered safe by washing in a solution of bleaching powder.

For more detailed methods of sampling foods, the reader is referred to Hamence and Taylor.[12]

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[12] Hamence and Taylor, *Chemistry & Industry*, **60**, 244 (1941).

IV. SCHEME OF ANALYSIS

GENERAL REFERENCES

Studinger, *Chemistry & Industry*, **56**, 225 (1937).
Hoogeveen, *Chemistry & Industry*, **59**, 550 (1940).
Degand, *J. pharm. Belg.*, **21**, 895 (1939).
Jacobs, *The Analytical Chemistry of Industrial Poisons, Hazards and Solvents.* Interscience, New York, 1941.
Maricq, *J. pharm. Belg.*, **21**, 749 (1939).
Analyst, **66**, 44 (1941).

A. SCHEME OF ANALYSIS

The detection of chemical warfare agents in the laboratory or, for that matter, in the field, resolves itself chiefly into the detection of traces of such war gases in soil, leaves, bricks, food, water, etc., which have been sprayed by the gas during action and of the air immediately above such materials.

The general method of procedure for the identification of a chemical warfare agent should follow the outline given below:

I. Organoleptic analysis
  1. Sight
  2. Sniff tests
  3. Other senses
  4. Physiological response

II. Chemical analysis
  1. Field Tests
    a. Test papers
    b. Test solutions
    c. Detector paints, powders and instruments
    d. Combustion methods
    e. Physical chemical methods
  2. Laboratory tests
    a. Air-flow analysis
    b. Analysis for a persistent lachrymator
    c. Analysis by a determination of the elements
    d. Determination of arsenic
    e. Confirmatory tests

As a rule, the tests should be made in the order given but, in many instances, a positive indication may eliminate the need for doing anything further than to perform a confirmatory test. Thus, if a sniff test indicates Lewisite and a rapid arsenic test is positive, none of the other steps need be taken. The contaminated materials other than foods must be decontaminated by procedures adequate for Lewisite pollution and foodstuffs must be destroyed. Similarly if the appearance of an object suggests contamination by mustard gas and the gold chloride field test is positive, analyses in the laboratory may be confined to confirmatory tests to estimate the degree of contamination.

Analysis for a persistent lachrymator should be performed only if the previous steps indicate a persistent lachrymator. It should rarely be necessary to perform analyses for the determination of the elements. In the majority of cases, sufficient definite information will be obtained from the preceding steps to proceed to the confirmatory tests at once.

The most important tests to be made are for the presence of the blister gases. In the case of foods and water, possibly the most important test is for the presence of arsenic, and ranking next in importance are the tests for mustard gas and for the identification of the individual contaminating arsenical compound.

It would seem desirable in the case of foods to establish tolerances for contaminants after taking into account the amount of gas which can safely be consumed at any one meal and the proportion of absorbed gas which is removed and detected by standard methods of analysis.

Special methods may be found suitable for particular materials and foods or for particular chemical warfare agents. Thus sugar may not interfere with many tests and an aqueous solution of contaminated sugar may be suitable for direct analysis. Dry materials in which but little hydrolysis can occur may be extracted with a suitable solvent.

I. Organoleptic Analysis

An organoleptic analysis or subjective examination is one in which the identity of a substance is determined by the use of one's senses. Thus, in identifying a war gas by its appearance, its odor and its physiological response, one makes use of the senses of sight, smell and the particular effect that a gas has on different organs of the body to come to some conclusion as to its nature. Organoleptic analysis or sensory detection is particularly important for the detection of war gases in the field where action is taking place, for under those conditions there are seldom other means of gas detection.

The principal senses used in the detection of chemical agents are those of sight and smell. The physiological effect of some of the war gases, especially the eye and nose irritants are also useful indicators of the identity of a gas.

1. SIGHT

The appearance of the gas cloud or smoke or of the chemical agent itself is sometimes an indication of the gas. The principal visible characteristics of the common war gases are given in Table 14. Thus a chlorine gas cloud is greenish-yellow in color; chloroacetophenone forms a bluish grey smoke from burning candles; diphenylaminechloroarsine forms a yellow smoke cloud while the substance itself may be greenish brown, etc. Of course, in order to see the color of the cloud, the gas inspector would have to be on the spot to see such evidence.

War gases leave other evidence of their presence. Chlorine, phosgene and diphosgene bleach the vegetation they impinge upon. Rotted clothing is evidence of such non-persistent agents or of the action of persistent agents like bromoacetone or mustard gas. Corroded metals, especially signs of corrosion on metals which ordinarily would show little signs of corrosion like copper or copper alloys, are evidence of contamination by acid war gases and screening smokes.

Black, brown or dark oily stains in a suspected area, are to be regarded with suspicion. Iridescent oil slicks, particularly on wet surfaces in a suspected area, may be an oily chemical agent like mustard gas. Moist foods show brown spots or other surface changes when contaminated by mustard.

The visible effect of poison war gases is also discussed in some measure in the chapter on the effect of chemical agents on materials and foods.

2. SMELL

It is advisable to make as little use of this sense as possible, particularly if one is not trained to smell correctly. The recognition of odors is acquired only with practice. Actually this test is a ***sniff test.*** One must never inhale deeply as in smelling a perfume, for actually only the nose has olfactory sense nerves. There is no need to fill the lungs merely to make a sniff test. Other precautions to be observed in making a sniff test are to sniff only once, then try to recall the odor. Repeated sniffs fatigue the olfactory sense organs and the sense of smell for that particular odor is soon lost. Flush the nose thoroughly by exhaling vigorously before any further attempts are made to use the sniff test again.

It is inadvisable to smoke before making a sniff test, as smoking also fatigues the olfactory nerves, but it is to be noted that chlorine, phosgene, hydrogen sulfide and hydrogen cyanide affect the taste buds in such a manner that tobacco smoke has a flat, metallic taste, making smoking rather unpleasant.

As indicated in Table 15, many of the war gases have characteristic odors which are detectable at very high dilutions. The concentration at which a

TABLE 14

APPEARANCE OF CHEMICAL AGENTS

CHEMICAL AGENT	COLOR AND STATE IN FIELD
Chlorine	Greenish yellow gas
Phosgene	First white, changing to colorless gas
Diphosgene	Oily colorless liquid
Chloropicrin	Oily liquid changing slowly in the open to a colorless gas
Phenylcarbylamine chloride	Pale yellow oily liquid
Dimethyl sulfate	Colorless oily liquid
Methylchlorosulfonate	Viscous liquid
Ethylchlorosulfonate	Colorless liquid
Ethylbromoacetate	Colorless liquid
Ethyliodoacetate	Colorless to brown oily liquid
Methylchloroformate	Colorless liquid
Bromoacetone	Colorless liquid
Bromomethylethyl ketone	Pale yellowish oily liquid
Chloroacetophenone	Colorless to brown crystalline solid, bluish grey smoke from burning munitions, colorless from shell
CNS	Colorless liquid changing to colorless gas
CNB	Same as above
Benzyl bromide	Colorless liquid
Xylyl bromide	Black liquid
Bromobenzyl cyanide	Oily brown liquid
Diphenylchloroarsine	Greyish smoke cloud
Diphenylaminechloroarsine	Yellow smoke cloud
Diphenylcyanoarsine	Greyish smoke cloud
Dichloromethyl ether	Colorless liquid
Mustard gas	Dark brown liquid changing slowly to colorless gas
Lewisite	Dark brown liquid changing slowly to colorless gas
Methyldichloroarsine	Colorless oily liquid
Ethyldichloroarsine	Colorless to yellow oily liquid
Phenyldichloroarsine	Viscous yellow liquid
Hydrogen cyanide	Colorless gas
Cyanogen chloride	Colorless liquid changing to colorless gas
Cyanogen bromide	White solid
Titanium tetrachloride	White smoke cloud
FS	Dispersed as liquid which changes to white smoke cloud
HC	White smoke produced by burning munitions only
White phosphorus	Dispersed as waxy solid which rapidly changes to flame and white smoke on contact with air

TABLE 15

MINIMUM DETECTABLE ODOR

SUBSTANCE	ODOR	AMERICAN DATA		BRITISH DATA*		SNEESSENS†	
		mg./l.	*ppm.*	*mg./l.*	*ppm.*	*mg./l.*	*ppm.*
Lung Irritants							
Chlorine	Highly pungent, like bleaching solution	0.01	3.5	0.01 –0.015	3.5–5.2	0.003	1
Phosgene	Musty hay, green corn, suffocating	0.004	1.0	0.005–0.01	1.2–2.5	0.001	0.25
Diphosgene	Ensilage, acrid, unpleasant			0.005–0.01	0.6–1.2	0.001	0.12
Chloropicrin	Flypaper anise sweetish	0.007	1.04	0.008	1.2	0.002–0.0025	0.3–0.37
Lachrymators							
Ethyliodoacetate	Pear drops			<0.001	<0.1		
Xylyl bromide	Elder leaves, pungent, aromatic			0.0003	0.04		
Bromoacetone	Pungent, stifling			0.005	0.9		
Chloroacetophenone	Apple blossoms	0.0001	0.016	0.0002	0.3		
Bromobenzyl cyanide	Sour fruit, burning						
Toxic Smokes							
Diphenylchloroarsine	Aromatic, shoe polish	0.0003	0.028	0.0003	0.028	0.0002	0.016
Diphenylcyanoarsine	Bitter almonds, irritant			0.00001	0.001	0.000005	0.0005
Vesicants							
Mustard gas (crude)	Garlic, horseradish, mustard	0.0018	0.28	0.0003	0.05	1–2	153.7–307.4
Mustard gas (pure)				0.001	0.15		
Lewisite (crude)	Geraniums	0.0014	0.17	<0.001	<0.12		
Lewisite (pure)				0.014	1.7		
Methyldichloroarsine	Fruity			0.0005–0.001	0.08–0.15		
Ethyldichloroarsine	Stinging, like pepper in nose	0.001	0.14	0.0008	0.11	0.00085	0.12
Systemic Poisons							
Hydrogen cyanide	Bitter almonds			0.001	0.9	0.0011	1
Cyanogen chloride						0.0025	0.6
Cyanogen bromide						0.0025	0.6
Hydrogen sulfide		0.001	0.75				

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* Ministry of Home Security, A.R.P.D., *The Detection and Identification of War Gases*. H.M.S.O., London 1939.

† Sneessens, J. pharm. Belg., **21**, 977 (1939).

gas becomes perceptible to the nose may be above or below a dangerous concentration. For example, the least perceptible odor of hydrogen sulfide is 0.75 part per million, whereas 100 parts per million are necessary to produce pronounced symptoms of eye and respiratory tract irritation. On the other hand, the least detectable odor of Lewisite is given by a concentration of 0.014 mg. per liter, which is far above the minimum irritating concentration of this agent, namely, 0.0008 mg. per liter.

Persons vary in their ability to detect and recall odors and in addition, olfactory fatigue sets in very rapidly. For instance, the ability to smell hydrogen sulfide is lost after 2 to 15 minutes exposure to 1–1.5 parts per million of that gas.

Too much reliance cannot be placed upon the sense of smell but where no other indicators are available and where one can use a gas mask, sniff tests are better than nothing.

One must always bear in mind that two war gases or mixtures of war gases may be used simultaneously to mask characteristic odors. In addition, a single chemical agent may be disguised by the addition of a harmless substance of strong odor with the purpose of causing confusion in attempting to recognize a war gas by its odor.

Procedure.—The war gas officer properly masked and clothed starting from the upwind side of the suspected area should walk to the point to be tested.

Remove the outer, anti-gas glove from the right hand if one is being worn or else remove the rubber glove. Take a moderately full breath, exhale a portion of the air breathed, and stop breathing. Stoop so as to bring the face as close to the ground or material as possible without touching any part of the person or equipment other than the feet to the ground. Insert two fingers of the right hand between the face and the facepiece of the mask near the cheek so as to permit air to enter at that point. Sniff gently but do not inhale. Resume the erect position. Recall the odor. Clear and reseat the mask, if necessary.

It is especially important to keep the gloved hand that is inserted into the mask free of any gas contamination else the sniff test will be vitiated and the gas officer may be hurt.

3. OTHER SENSES

Little use of the senses other than those of sight and smell is made. Actually the "tobacco reaction" mentioned in the previous section is a taste test although it is greatly influenced by the olfactory sensations.

Sometimes, especially in the field, a chemical shell containing a liquid can be distinguished from other shell by the peculiar intermittent whirring noise it makes in flight and usually by its low detonation sound.

4. PHYSIOLOGICAL RESPONSE

The physiological effects of war gases are often sufficient for the subjective detection of these agents. This is particularly true of the eye and nose irritants. In some instances, as for example, in the case of chloroacetophenone or other non-toxic tear gas, the copious weeping induced by the agent is sufficient evidence of its presence.

Any test depending solely on the physiological effect of a war gas is to be regarded with disfavor, because the insidious character of some of the gases prevents recognition of the extent of danger until serious damage results. This is especially true of the lung irritants and the vesicants, which are the most efficient casualty agents. For example, the immediate irritation produced by phosgene is mild compared to that caused by an arsenical smoke like diphenylaminechloroarsine, or a tear gas like chloroacetophenone. Nevertheless, a person who appears to be only slightly gassed by phosgene may become a serious casualty several hours later, while a person apparently severely gassed by the toxic smoke or tear gas will probably recover almost completely after a relatively short interval. One must always bear in mind that a persistent lachrymator may merely be the mask for a more dangerous vesicant.

As an illustration of the good warning power of some of the chemical agents, one may consider chloropicrin. This substance has a minimum lachrymatory concentration ranging from 0.29 to 2.8 parts per million, whereas the minimum lethal concentration for an exposure of 10 minutes is nearly 300 parts per million or roughly 100 times as much as the maximum necessary to induce weeping.

II. Chemical Tests

Chemical tests which can be performed in the field are desirable for the detection of war gases. Unfortunately, because of the diverse character of the war gases, there can be no single test which will detect all of the war gases. However, there are certain field tests available by which one is able to divide chemical agents into a few groups. The principal field group tests are those which show the presence of a halogen compound or the presence of an acid on hydrolysis of the war gas. Other important group tests are those which show a change in color with sulfuric acid and those which show the presence of cyanide or arsenic or both.

An adequate field test is one which is simple, specific, delicate and preferably rapid. Most of the field tests which have been devised for the purpose of detecting war gases are based upon the change in color of a test paper, a detector paint, or of a test reagent, although some physicochemical methods have also been advocated. These tests are generally

TABLE 16

PHYSIOLOGICAL EFFECTS OF WAR GASES

CHEMICAL AGENT	IMMEDIATE PHYSIOLOGICAL EFFECT
Chlorine	Choking, coughing, smarting of eyes and discomfort in chest
Phosgene	Choking, coughing, pains in chest, immediate effects not severe, later effect may be very serious
Diphosgene	Similar to above, somewhat greater lachrymatory effect
Chloropicrin	Lachrymation, nose and throat irritation, vomiting
Phenylcarbylamine chloride	Throat, nose and eye irritation
Dimethyl sulfate	Lachrymation, irritation of mucous membranes and skin
Methylchlorosulfonate	Throat and eye irritation
Ethylchlorosulfonate	Throat and eye irritation
Ethylbromoacetate	Eye and throat irritation
Ethyliodoacetate	Eye irritation
Bromoacetone	Eye and skin irritation
Bromomethylethyl ketone	Eye irritation
Chloroacetophenone	Eye and skin irritation
CNS	Eye, skin and throat irritation, nausea
CNB	Eye and skin irritation
Benzyl bromide	Irritation of the eyes and mucous membranes
Xylyl bromide	Eye irritation
Bromobenzyl cyanide	Severe eye irritation
Diphenylaminechloroarsine	Headache, vomiting
Diphenylchloroarsine	Headache, vomiting, sneezing
Diphenylcyanoarsine	Headache, vomiting, sneezing
Dichloromethyl ether	Throat irritation
Mustard gas	None
Lewisite	Nose and throat irritation
Methyldichloroarsine	Irritation of respiratory tract
Ethyldichloroarsine	Irritation of respiratory tract
Phenyldichloroarsine	Irritation of respiratory tract
Cyanogen chloride	Eye irritation
Cyanogen bromide	Eye irritation
White phosphorus	Glow from burning particles, dense smoke, incendiary effect
HC	Slight suffocating feeling, dense smoke
FS	Prickly sensation on skin, eye irritation, dense smoke
Titanium tetrachloride	Very slight irritation of eyes, dense smoke

sufficiently simple, delicate and rapid. They are seldom specific, however, and therefore need confirmation and interpretation.

Nitrogen oxides, carbon monoxide and other decomposition products of high explosives, chlorine and the paralysants hydrogen cyanide and hydrogen sulfide should be tested for in the field by sampling the air above a contaminated spot, for by the time the sample is taken to the laboratory, these substances will be dissipated. Phosgene may be detected in the laboratory sample if it remains with its solvent, such as "Tetra", soaked into the test sample. Since it is lost in the ether extraction and evaporation, it is better to test for phosgene in the air above the sample.

1. FIELD TESTS

a) Test Papers

Possibly the simplest form of field test available is the one based on the change in color of a test paper. The individual test papers and their preparation are described in Chapter VI under the particular compound for which their use is designed. The principal papers and the substance which they are used to detect are given in Table 17.

There are three basic methods used in employing tests papers. These are: (1) drawing the air through the test paper; (2) suspending the paper in the atmosphere or the stream of air to be tested; and (3) immersing the paper in a suspected liquid or extract of the suspected material. The first method almost always requires an aspirator of some kind. For field use, three simple types of aspirating devices are available; they are (a) rubber bulb aspirator, (b) hand pump and (c) aspirator bottle or can.

Aspirators.—*Aspirator Bulb.*—Aspirator bulbs are rubber bulbs which have two valves. When the bulb is squeezed, the air or gas is expelled through one valve while the other valve is closed. On the release of the pressure, the first valve closes while the second valve opens admitting more gas or air. These bulbs ordinarily have a capacity of about 40 to 60 ml.

Aspirator bulbs are simple to use and carry. They can be used almost anywhere. However, the rubber ages, so that these bulbs become less efficient with use. The valves leak, at times, because dirt accumulates and lodges in the valve seat. Sometimes this can be remedied by removing the dust and wetting the valve seat. The greatest disadvantage of these bulbs is that the use of them is extremely tedious and fatiguing.

Hand Suction Pump.—The British Department of Scientific and Industrial Research has adopted as the official sampling device, a hand exhausting pump, with a barrel of approximately 1.25 inch bore and a capacity of 126 ml. To the inlet end of the pump is screwed a spigot with an external screw 7/16 inch, outside diameter, 0.437 inch, having 14 threads per inch according to the American National coarse thread dimensions system. To this is screwed a special holder, Fig. 1, containing a test paper or the sampling train is attached if an absorber is used. On the upward stroke, the air to be sampled is drawn through the test paper or test solution and is expelled on the downward stroke by a system of valves analogous to the bulb aspirator. The strokes should be slow and steady and a counter may be attached so that the number of strokes made can be read from the counter.

TABLE 17
TEST PAPERS

TEST PAPER	POSITIVE COLOR COLOR CHANGE	DETECTS
Starch-potassium iodide	Blue	Chlorine, bromine and in general oxidizing agents
Fluorescein-potassium bromide	Red	Chlorine, bromine
o-Tolidine	Yellow orange	Chlorine
Mercurochrome	Yellow	Halogens
Fluorescein	Rose	Bromine
Fuchsin-sulfurous acid	Violet	Bromine
p-Dimethylaminobenzaldehyde diphenylamine (Harrison)	Yellow or orange	**Phosgene,** chloromethylchloroformate, **diphosgene** and hydrochloric acid
1,3,6 Nitrodimethylaminophenol-*m*-diethylaminophenol	Green	**Phosgene**
Lead acetate	Black	Hydrogen sulfide
Gold chloride	Yellow or brown red	**Mustard gas**
Sudan red	Blood red	**Mustard gas**
Sodium iodoplatinate	Purple red then blue	**Mustard gas**
Benzidine-copper acetate	Blue	Hydrogen cyanide, chlorine
Methyl orange-mercuric chloride	Pink	Hydrogen cyanide
Picric acid-sodium carbonate	Red	Hydrogen cyanide
Sodium sulfide (later $FeCl_3$)	Red	Cyanogen bromide, cyanogen chloride
Dimethylaniline	Yellow or brown	**Chloropicrin**
Mercuric bromide or mercuric chloride	Yellow or brown	Arsine
Silver nitrate	Black	Arsine, white phosphorus
Cuprous paper	Red	**Lewisite**
Palladium chloride	Grey	Carbon monoxide
Congo red	Blue	Acids
Acid-base indicators	Acid color	Acids

Other hand pumps are described by Viles,[1] Haldane,[2] and Lee.[3] The pump designed by Lee can also be used as a gas sampler, for when it is clean, dry and air tight, it will store dry air approximately 24 hours without measurable change in carbon dioxide or oxygen percentage.

Aspirator Can.—Where neither a rubber bulb aspirator or hand pump is available or for other reasons cannot be used, a simple type of wet form aspirator can be made from a gallon or larger volume tin can.

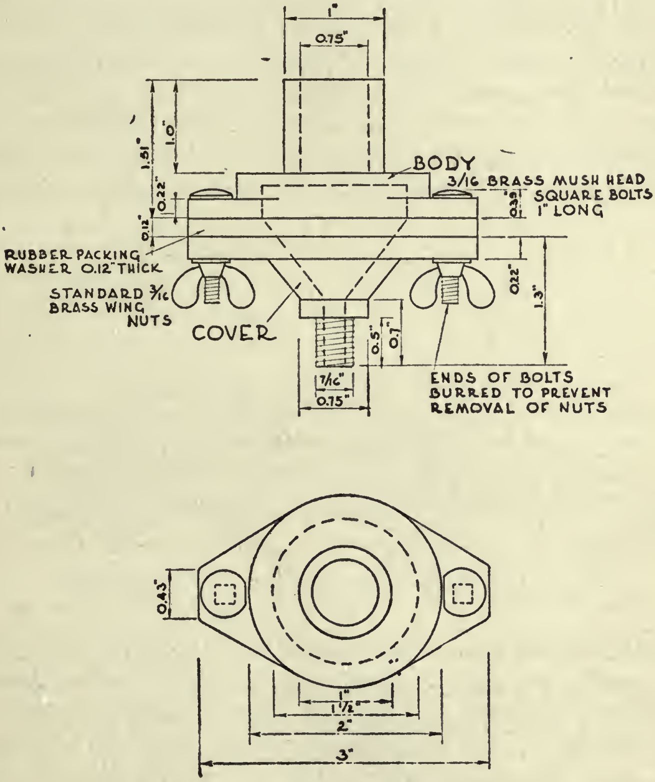

FIG. 1. Test Paper Holder

Puncture a hole close to the bottom in the side of a tin can and insert a stopcock, or a rubber stopper fitted with a glass exit tube to which is attached a rubber tube and a pinch or screw clamp. Of course, if the exit cock can be soldered in, so much the better. In the mouth of the can insert a rubber stopper with an entrance glass tube which is connected with the test paper holder or test bottles.

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[1] Viles, *J. Ind. Hyg. Toxicol.*, **22**, 188 (1940).

[2] Haldane, and Graham, *Methods of Air Analysis*. Griffin, London, 1935.

[3] Lee, ***Ind. Eng. Chem., Anal. Ed.*** **5**, 354 (1933).

By filling the can with water, and allowing the water to flow out of the exit stopcock, or tube, air can be drawn into the can and hence through the sample and the test paper.

The can may also be used by arranging a siphon system, in which case no stopcock need be attached to the tin can itself.

The great advantage of a water aspirator of this type is that a continuous stream of air can be sampled while the operator is performing other duties.

Test Paper Holders.—In making a test in which the air or atmosphere to be analyzed is drawn through a test paper, some means must be provided to hold the paper. Fig. 1 shows a test paper holder which is used with a hand pump. This is a machined piece of aluminium, consisting of a lower section, a packing washer and a cover. The test paper is inserted in the holder and is held in place by tightening the wing bolts.

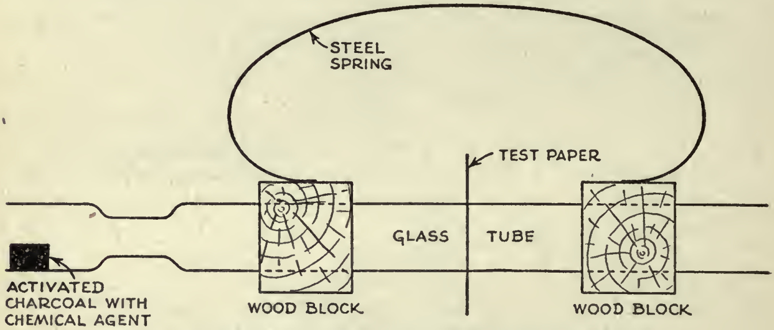

Fig. 2. Dijkstra Apparatus and Test Paper Holder

Another type of test paper holder is described by Clarke and Hermance.[4] The unit consists of a pair of glass tubes, the ends of which terminate in heavy face-ground flanges, the plane of grinding being exactly normal to the axis of the tube. The flange openings have the same bore as that of the tube. Such flanges may also be turned from Pontalite rod, thereby obtaining the advantages of accurate machining. The paper is inserted between the flange faces, and pressure is applied by a clamp assembly.

A simpler device, though probably not as efficient, is described by Dijkstra[5] and by Hoogeveen.[6] Two flush ground glass tubes are held together by means of wooden blocks attached to a spring as shown in Fig. 2. The paper is held in place by the tension of the spring and is inserted by allaying the tension.

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[4] Clarke and Hermance, *Ind. Eng. Chem., Anal. Ed.* **10,** 591 (1938).

[5] Dijkstra, *Chem. Weekblad,* **34,** 351 (1937).

[6] Hoogeveen, *Chemistry & Industry* **59,** 550 (1940).

Lachele[7] describes a test paper holder in which a disk of paper is placed between two thick-walled tubes of the same diameter with ground glass ends held together by an outside sleeve of rubber tubing. One may make a similar type test paper holder out of an adapter with a ball and socket joint. The disk of test paper is placed on the socket section and then the ball section is inserted, after which the clamp with which most of these joints are fitted is put into place. For most purposes this will be an adequate device. Other devices for holding test papers are described by Stubbs[8] White[9] and Yagoda.[9a]

Procedure.—(1) Place the test paper, moist or dry as the case may be, in the holder and attach to the aspirator device. Draw the air or the atmosphere to be sampled through the paper or through the sample and then through the paper by alternate compression and decompression of the aspirator bulb, by stroking the pump or by allowing a slow stream of water to flow from the aspirator can. After a volume of air equivalent to 25–50 compressions or strokes have been made, remove the paper and examine. Positive changes in color are mentioned in Table 17.

(2) A simple method for suspending not only one test paper but a series of test papers is described by Maricq.[10] His apparatus consists of a wide mouthed glass bottle stoppered with a rubber stopper equipped with an entrance and exit glass tube. One of these tubes is long enough to reach almost to the bottom of the bottle and is connected by means of a rubber tube to a bulb aspirator, a hand pump or an aspirator can. On the bottom of the stopper there are a series of catches or hooks from which the test papers may be suspended. A small amount of wet absorbent cotton placed on the bottom of the bottle supplies the humidity necessary for some of the reactions. Such a device can easily hold four or more papers.

Draw the air through the bottles in which the papers are suspended and note the change in color.

Even simpler though not nearly so good as the above is the mere suspension of a series of test papers in the suspected atmosphere or in a stream of the air to be tested or over a test tube.

(3) The third procedure is self-explanatory. Dip the test paper into the solution to be tested and note the color change.

b) *Test Solutions*

Test solutions are less convenient to use in the field than test papers. However, they are less likely to yield dubious results and are more likely

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[7] Lachele, *Ind. Eng. Chem., Anal. Ed.*, **6**, 256 (1934).

[8] Stubbs, *Analyst*, **52**, 699 (1927).

[9] White, *Analyst*, **52**, 700 (1927). [9a] Schleicher and Schull Co., New York, Bull. No. 2 (1942).

[10] Maricq, *J. pharm. Belg.*, **21**, 749 (1939).

to be specific reagents. Most of the test solutions used are simply modifications of the reagents used in the laboratory for the confirmation of the presence of a chemical agent. These reagents are described in Chapter VI under the substance for which their use was developed.

As an illustration of how to proceed in making a test in the field, we may take a method for detecting the presence of mustard gas.

Mustard Gas Test.—The war gas inspector must have, in addition to the equipment and anti-gas clothing noted on page 55, a metal suction, hand pump fitted with a right-angle adapter, some sampling tubes containing glass wool moistened with dilute acetic acid, a dropping bottle containing sodium iodoplatinate solution, a dropping bottle containing starch solution, and some cloth-diaphragmed sampling funnels. The gas officer and his assistant properly clothed should go upwind of the contaminated area, or the suspected area, and should follow the procedure carefully. The test apparatus is shown schematically in Fig. 3.

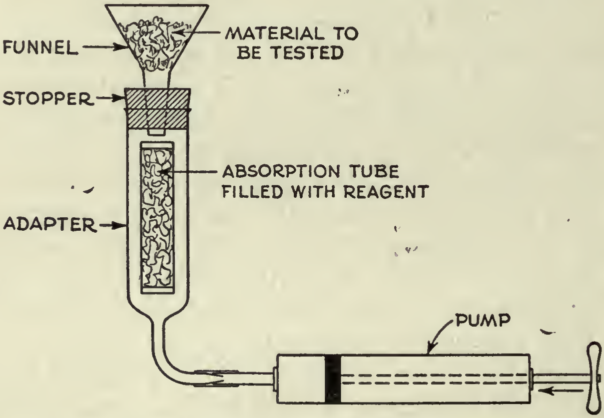

Fig. 3. Schematic Diagram of Field Apparatus for Mustard Gas

Procedure.—Take the suction pump and hold it uppermost in the left hand. With the other hand open the equipment case, and insert a sampling tube into and a sampling funnel over the pump adapter. Remove a sampling spatula and close the case. Holding both pump and spatula in the left hand, slip an anti-gas glove over the rubber glove on the right hand with the aid of an assistant, transfer the spatula to the right hand and walk to the contaminated area, selecting, as far as possible, a part of the latter where the surface material is loose enough to be dug out with the spatula. If, however, the material is a hard surface, soak up any visible drops with the aid of filter paper and a forceps.

Partially fill the sampling funnel with the material to be tested, lay the spatula on the ground, and aspirate 40 strokes of air through the sample, still holding the pump in the left hand and working the handle with the doubly gloved right hand. Subsequently remove the sampling funnel from the end of the adapter, place it on the ground and walk back to the original position upwind of the contaminated area, being careful not to carry any contamination along by wiping the feet in dust, doormat fashion. Slip off the outer glove from the right hand with the aid of the assistant, open the equipment case with this hand and by means of the dropping bottles, transfer 2 drops of sodium iodoplatinate solution followed by 2 drops of starch solution to the sampling tube in the adapter. Finally, take the sampling tube out of the adapter with the right hand, give it one sharp shake and observe the color. See page 114 for reagents.

If a blue color is present, mustard gas is indicated. If a positive result is obtained, it should be reported at once. If a dubious result is obtained, a sample of the material should be taken as directed on page 55 for analysis in the laboratory. If the color of the reagent turns pale, Lewisite or some other reducing agent may be present.

Sample Tubes.—To prepare the sample tubes for the field testing of mustard gas, insert a lightly packed wad of glass wool, approximately 0.1 gram in weight into each tube, moisten with a few drops of 5 per cent acetic acid, allow to drain for some minutes and remove any liquid in the tip of the tube with the aid of filter paper before it is placed in the sampling case. To prepare the 5 per cent acetic acid, add 5 ml. of C. P. acetic acid, free from reducing impurities to 95 ml. of distilled water and mix thoroughly.

Another field sampling device is shown in Fig. 4. It is best to mount this apparatus in a box. Drawing strokes with the hand suction pump forces the air to be tested through the reagent or absorbing solution. The reaction may be noticed in the field if a reagent solution is used, or else the tube may be stoppered and the absorbing solution may be analyzed later in a laboratory. The trap is used to protect the pump.

Still another field test method is described on page 114 in which a pear-shaped glass bulb, having a narrow-bore U-tube at its lower extremity, is used as the absorbing vessel. The narrow U enables one to pass a relatively large volume of air through a small volume of liquid. The test described is designed to detect mustard gas by means of gold chloride solution, but the equipment may be used for other war gases by changing the reagent.

Field Kit.—A small field kit, 8.5 x 5.5 x 2.5 inches, has been devised by Defrance[11] for the rapid detection and identification of war gases. This kit is limited in its application, of course, but a description will enable the reader to see the relatively wide range of a small kit. It contains the following reagents and equipment in various compartments:

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[11] Defrance, *J. pharm. Belg.*, **22**, 197 (1940).

1) A test tube and 2 small metal boxes containing Sudan Red powder for testing for mustard gas.

2) Bottle of distilled water, an aspirator bulb and a rubber tube.

3) A series of reagents in pipette form dropping bottles containing:

a) Methyl orange + methylene blue indicator for detecting hydrolyzable compounds like phosgene and the chlorinated ethers, see page 85.

b) Harrison's reagent, *p*-dimethylaminobenzaldehyde + diphenylamine for detecting phosgene, see page 103.

c) Solution of dimethylaniline in benzene for chloropicrin, see page 123.

d) Sodium sulfide solution for cyanogen bromide and chloride, see page 122.

Spare pipette droppers and bands of filter paper are kept behind the reagent bottles.

4) The cover carries another series of reagent bottles stoppered with corks equipped with short glass rods for spotting on reagents.

a) Lead acetate solution for hydrogen sulfide.

b) A bottle of picric acid solution and another bottle of sodium carbonate solution for hydrogen cyanide.

c) Universal indicator solution.

d) Two small vials containing solid potassium permanganate and palladium chloride, the latter for the detection of carbon monoxide.

5) A small lamp with a copper spiral to be used for detecting the presence of halogen compounds by the Beilstein test, see page 85.

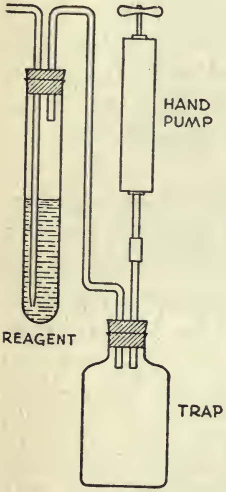

Fig. 4. Field Sampling Device

Procedure.—The pipette form droppers are used in the following manner: Draw one drop of reagent from a reagent bottle with the aid of the pipette dropper. Invert the dropper so that the drop of reagent flows toward the rubber nipple. Press the rubber nipple so that the air is expelled and while compressed, hold the pipette dropper in the normal position to allow the drop to flow back to the tapered end. Let the air to be tested enter slowly by cautiously releasing the pressure on the rubber nipple so that it will splash through the bubble. By repeating the operations over again, with the same reagent drop, a greater volume of air can be tested.

Separate a band of filter paper into sections by impregnation with paraffin at vertical intervals along the band. Impregnate each section with the reagent solutions. Place the band in the test tube. Along side of the band place a glass tube, long enough to reach to the bottom of the test tube, connected to the rubber aspirator by means of the rubber tube. Hold the glass tube in place by means of a notched cork. Draw the air to be tested through the notch across the test paper by the action of the aspirator bulb and note the changes in the impregnated filter paper.

c) *Detector Paint and Powder*

One of the methods of detecting mustard gas spray or splashes is to use detector paints. These paints are relatively secret paint mixtures that can be bought only from government licensed establishments or are supplied by the government.

Surfaces covered with this paint, which has a yellowish color, will turn reddish if *liquid* or spray of mustard gas comes in contact with it. Certain liquid lachrymators also cause this change in color but one should be able to differentiate because of the physiological reaction produced by the tear gas. However, the possibility of a mixture should not be ignored. The vapor of war gases has no effect on these detector paints and therefore the use of these paints is relatively limited.

It should also be noted that certain organic solvents, such as acetone and pyridine also produce a red color when in contact with the paint and moreover, that heat will cause a color change.

Paint detectors must be used with the fixed idea of confirming the presence of gas by some more adequate means. In other words they are indicators only.

A variation of detector paint is the incorporation of a gas indicator with gelatin, agar etc. The indicator mixture is allowed to set in a tube. Some of the sample and a little of a solvent like trichloroethylene or tetrachloroethane is added. Then a change in color is observed.

Sudan Red Test.[12]—Sudan Red powder* may be used to detect mustard gas by dusting directly over areas suspected of contamination by this agent. A blood-red color indicates a positive reaction. The powder is to be preferred to the use of paper impregnated with the dye, because contact between the gas and the reagent is facilitated physically and the contrast in colors before and after reaction is more marked.

Procedure.—Grind 1 part of Sudan Red with 1000 parts of ground chalk. Mix this well ground powder with 3000 parts of non-purified sea

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[12] Ligtenberg, *Pharm. Weekblad*, **74**, 185 (1937); *Chem. Weekblad*, **34**, 321 (1937); *Analyst*, **62**, 326, 572 (1937).

* According to the *Colour Index* of the Society of Dyers and Colourists, 1924 edition, there is only one Sudan Red. Its *Colour Index* number is 857 and its Schultz and Julius number (1923 edition) is 694. Sudan Red is a mixture of aminonaphthyldinaphthazonium chloride and diaminonaphthyldinaphthazonium chloride.

sand. The sand is not essential but enables the dye to be distributed more easily over a larger area. If a positive reaction results, dust another powder containing 1 part of ferric chloride and 7 parts of ground chalk over the first powder. A green color is obtained in 1 minute if mustard gas, bromobenzyl cyanide, or phenylcarbylamine chloride, which are used to mask the mustard, are present. The test is not specific. Carbon dioxide, fatty oils, chloropicrin and diphosgene produce a rust-colored stain, which may turn green over a long period. Benzene and lubricating oils, which may occur on the roads in large cities, do not react. The ferric chloride powder is hygroscopic and should be stored in a suitable container. It should be used on surfaces like paving stones which are not too porous, as a dry porous stone can prolong the period of reaction by 30 minutes. Sudan Red test paper alone is affected by other vapors than mustard gas, namely, petroleum, benzene, chloropicrin, alcohols and fatty substances.

A greyish white detector powder developed in Czechoslovakia is said to be able to distinguish mustard gas, Lewisite and phosgene. It turns red in the presence of mustard gas, orange in the presence of Lewisite and deep blue in the presence of phosgene. It is not affected by lachrymators or by oils. It is claimed to be very sensitive. Thus, it is said to be capable of detecting concentrations of mustard gas of the order of 50 mg. per square mile.

d) Combustion Methods

Since many of the common war gases are halogen compounds, combustion methods may be used to detect their presence. In some of these methods, the suspected atmosphere is passed through a bubbler containing ethyl or amyl alcohol. A portion of these absorbing solutions is burned in a special lamp and the combustion products are trapped in either silver nitrate or sodium hydroxide solution so that the chloride, bromide or iodide formed may be detected and estimated by silver nitrate.

Another of these methods is based on the principle that the vapor of chlorinated hydrocarbons mixed with moist air is decomposed quantitatively into hydrogen chloride when passed through a silica tube heated to 1000–1100° C., or at 850° C. if catalyzed by platinum foil. By absorption and estimation of the hydrogen chloride formed, the concentration of chlorinated hydrocarbon in air may be calculated. If water vapor is not present in sufficient amount, small quantities of chlorine are produced. This method is difficult to use in the field, since such high temperatures are required. The details of these methods are given by Jacobs.[13]

Since dimethyl sulfate, hydrogen cyanide and diphenylcyanoarsine contain no halogen, they cannot be detected by such methods.

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[13] Jacobs, *The Analytical Chemistry of Industrial Poisons, Hazards and Solvents.* Interscience, New York, 1941.

A combination of the combustion method and test paper method is described by Twiss[14] and others.[15] The atmosphere to be tested is burned in a special ethyl alcohol lamp. Any halogen compound present is detected by the appearance of the flame (see Beilstein test, page 85). Any sulfur present is converted to sulfur dioxide. The combustion gases are permitted to pass up a chimney and impinge on a test paper impregnated with phosphotungstic-phosphomolybdic acid prepared as directed below. A positive test for both elements, which are characteristic of mustard gas, may indicate that compound. Chlorosulfonic acids will also give positive tests for both elements.

To make the test paper reagent, boil 10 grams of sodium tungstate, 2 grams of phosphomolybdic acid, 10 grams of syrupy phosphoric acid, and 70 ml. of water for 2 hours. Cool, filter and make up to 100 ml. This solution will last for a year. Soak paper in the reagent, dry in subdued light and keep in the dark.

To use the paper, hold it across the chimney of the lamp and spot on 6 *N* ammonium hydroxide solution. Sulfur compounds form a deep blue ring on the damp spot.

"Telltale" Lamp.—A simple combustion indicator can be made from an ordinary kerosene automobile tail light lamp provided with a coil of copper wire suspended in the flame. Alcohol is preferable as a fuel when this lamp is used for the detection of war gases. It is used principally for the detection of phosgene. The air is drawn in at the base of the lamp around the flame and copper wire. If a halogen bearing war gas is present, the flame acquires a very distinct green color. Phosgene may be detected in concentrations of the order of 0.3 mg. per liter.

e) *Physical Chemical Methods*

Methods depending upon the index of refraction of an atmosphere; upon the change in conductivity or pH of a solution after absorption of noxious materials from an atmosphere; on the absorption of radiant energy; on the vapor pressure developed after freezing a contaminant from the air; on passage of the air through silver nitrate solution, then determining the turbidity caused by silver chloride, etc. nephelometrically have been suggested as means for the detection of chemical agents in the field. Most of these methods are not sufficiently sensitive or are too complicated to be used for field work.

2. LABORATORY TESTS

For a chemical analysis, a sample should be taken as described in the foregoing sections from the exposed surfaces of the contaminated material.

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[14] Twiss and Neale, *Chemistry & Industry*, **59**, 13 (1940).

[15] Edwards, *Chemistry & Industry*, **59**, 239 (1940).

Wherever possible, it is of great help to secure a sample of the actual liquid contaminant by absorption of the droplets and splashes on absorbent cotton or filter paper.

It will generally be unnecessary to observe the extreme personal precautions necessary for sampling in the laboratory. Nevertheless great care must be used. The manipulative work must be performed in a well-ventilated fume hood. Non-permeable or impregnated gloves and a gas mask, if necessary, should be worn while doing the work. All apparatus employed in the analysis must be decontaminated immediately after use to destroy all traces of the war gases, not only to make sure that subsequent analyses will be correct but also for personal protection. For the destruction of most gases, treatment with hot alcoholic potassium hydroxide solution is adequate, but for certain gases other reagents are better. Thus Lewisite, for instance, is rapidly decomposed by cold aqueous alkali. For glassware contaminated with mustard gas, washing with concentrated nitric acid is the most convenient laboratory procedure. Rubber connecting tubes, forceps, etc. should be boiled for 30 minutes in water, and rubber gloves for 2 hours to decontaminate them from mustard gas.

If a sample contaminated with a vesicant comes into direct contact with the hands or skin, the affected areas should be scrubbed immediately as thoroughly as possible several times with soap and hot water.

The presence and character of a poison gas in a material significantly contaminated by such substances will be evident by organoleptic analysis, that is by the subjective indications described in previous sections. In such instances of gross contamination, no full analysis need be made. The entire lot from which the sample was taken should be destroyed, or submitted to decontamination or salvage treatment, according to the case and the type of contamination.

The possibility of mixed gases being used should always be borne in mind. For instance, sulfuryl chloride was used during the World War 1914–1918 in combination with phosgene, chloropicrin, and cyanogen chloride to make those toxic agents visible. Hydrogen cyanide was used with arsenic trichloride (Vincennite) or tin tetrachloride to prevent polymerization of the former. Still other mixtures, such as chloropicrin and arsenic trichloride, mustard gas and Lewisite, chloropicrin and bromobenzyl cyanide have been suggested. A persistent lachrymator, like ethyliodoacetate, may be used to mask the characteristics of a more dangerous agent, such as mustard gas. Even butyl mercaptan, an ingredient of stink bombs, nitrobenzene, citronellol and amyl acetate have been used to mask the presence of casualty agents. For this reason, the absence of dangerous vesicants should always be established chemically when contamination with a persistent tear gas or a masking odor is found.

New or Surprise War Gases.—It is a function of the war gas inspector to indicate the possibility of a new war gas. It is the function of the chemist to detect and identify any new or unusual chemical agents. Chloroformoxime $ClCH:NOH$, dichloroformoxime $Cl_2C:NOH$ (phosgene oxime) tetraethyl lead $Pb(C_2H_5)_4$, cyanogen fluoride CNF, diethyl telluride $(C_2H_5)_2Te$, tetrachlorodinitroethane $C_2Cl_4(NO_2)_2$, prickling gases which set up an intolerable itching or orticant action like *o*-chlorobenzalmalonodinitrile, $ClC_6H_4CH=C(CN)_2$, nitroxyl fluoride, NO_3F, methyldifluoroarsine CH_3AsF_2 (analogous to methyldichloroarsine) and selenium oxychloride $SeOCl_2$ have been mentioned as possible chemical warfare agents.

a) Air-flow Analysis

In this method purified air is passed through the suspected material and into an absorbing solution. Some of the contaminant will be carried by the stream of purified air into the absorbent, which is then subjected to a series of tests to identify the chemical agent. The advantage to be obtained from some system of air-flow analysis is that the unchanged gas may be recovered from the material. Its most serious disadvantage is that only a very small proportion of a chemical agent may be removed when the volatility is very low or when some loose chemical combination has taken place. As Page[16] points out, even readily volatile substances are retained firmly by many foods. For instance, ethylene oxide, b. p. 12.5° C., and hydrogen cyanide, b. p. 26° C. are removed only to the extent of 10 per cent or so of the total amount absorbed by aeration alone. Elevation of the temperature will assist in the recovery of the less volatile chemical agents.

The sensitivity of the method may be widely varied by altering the design of the apparatus, the rate of air passage, and the efficiency of the absorptive system, as well as by modifying it to include condensation on charcoal or similar adsorbent from which the gas can subsequently be expelled. The sensitivity of some of the systems appears to be too low, since positive tests are obtained with difficulty from food contaminated by liquid mustard gas and Lewisite, which smells noticeably of these substances.

It is best in performing an air-flow analysis to use only one reagent absorbent at a time and not a series of absorbents.

Absorption in Water.—Place approximately 20 grams of the sample to be examined, cut up into small pieces, in a large glass tube, 6 inches long

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[16] Page, *J. Roy. Sanit. Inst.*, **61**, 155 (1941).

by 2 inches wide, or a similar device fitted with a standard taper stopper equipped with right-angled glass inlet and outlet tubes, the former leading to within 2 cm. of the bottom of the tube, as illustrated in Fig. 5. A tube fitted with all-glass interchangeable connections is to be preferred but rubber stoppers may be used. Surround the tube by a water bath maintained at 37° C. Draw air purified by passage through a tower or U-tube containing granular activated charcoal and dried by passage over anhydrous calcium chloride in another U-tube or tower, for 10 to 15 minutes at the rate of 0.1 to 0.5 liter per minute through the sample in the tube into 10 ml. of absorbent in a bubbler. In carrying out the preliminary sorting tests, first aspirate into water, and examine the aqueous solution so obtained, after warming and cooling by the scheme outlined in Table 18.

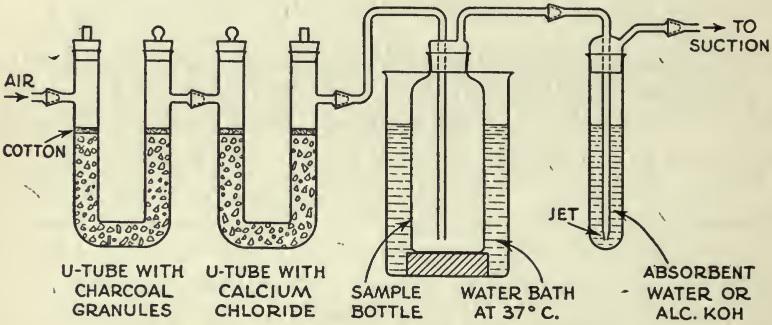

Fig. 5. Apparatus for Air-Flow Analysis

Absorption in Alcoholic Potassium Hydroxide Solution.—Repeat the aspiration using alcoholic potassium hydroxide solution as the absorbent. Examine several portions of the alcoholic potassium hydroxide solution after warming and cooling by the scheme outlined in Table 19.

Apply the confirmatory tests described in Chapter VI, page 99, based on the preliminary indications obtained above, using the air-flow procedure whenever practicable. It should be noted that in air-flow analysis chemical agents such as chloroacetophenone and the arsenical smokes will not vaporize appreciably, and that very little vapor may be given off by the relatively non-volatile liquid gases such as bromobenzyl cyanide, xylyl bromide, etc. Moreover, if the material under examination is wet, any agent present may be hydrolyzed, in which case air-flow analysis may yield little information.

Adsorption on Silica Gel.[17]—Information as to the identity of a war gas

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[17] Hoogeveen, *Chemistry & Industry*, **59**, 550 (1940).

TABLE 18

ANALYSIS OF THE AQUEOUS SOLUTION AFTER ASPIRATION

PROCEDURE	RESULT	INDICATION
Filter if necessary* and test a portion of filtrate with $AgNO_3$ solution	White precipitate of AgCl	**Mustard gas, Lewisite, Diphosgene** or other readily hydrolyzable agents, see pages 85 and 140
If a precipitate is obtained with $AgNO_3$, test other portions as follows:		
(1) Add a few drops of H_2S water	Turbidity† Turbidity, soluble in excess	Alkyl dichloroarsines **Lewisite**
(2) Add a drop of 1% phenol solution and overlay with concentrated H_2SO_4	Red zone at interface due to formaldehyde	Chloromethylchloroformate, halogen substituted methyl ether
(3) Add NaOH solution and warm	NH_3 evolved	Cyanogen halide
(4) Add $BaCl_2$ solution	White precipitate of $BaSO_4$‡	Chlorosulphonic acid and esters, sulfuryl chloride, etc.
(5) Add $Pb(Ac)_2$	Black precipitate of PbS	Thiophosgene, perchloromethyl mercaptan
(6) Reduce with Zn and HCl	AsH_3 evolved	$AsCl_3$, **Lewisite** and analogous arsines may yield arsine under these conditions

NOTES: * Precipitate may be a gelatinous hydroxide obtained from some adjuvant such as the tin, titanium or silicon tetrachlorides, diphenylurea from phenylcarbylamine chloride or sulfur from perchloromethyl mercaptan.

† Cyanogen chloride or bromide may give a precipitate of sulfur, and phenylcarbylamine chloride may yield an oily suspension of phenylisothiocyanate.

‡ A precipitate of barium sulfate without an accompanying chloride precipitate indicates sulfur trioxide or dimethyl sulfate.

TABLE 19

ANALYSIS OF ALCOHOLIC POTASSIUM HYDROXIDE ABSORBENT SOLUTION

PROCEDURE	RESULT	INDICATION
(1) Acidify with HNO_3 add $AgNO_3$ solution	Pale yellow precipitate of AgBr	Tear gas containing bromine like **Bromobenzyl cyanide**
(2) Add nitrite reagent, page 123 or acidify with HAc and add Griess-Ilosvay reagent, page 123	Pink or red color	**Chloropicrin**
(3) Acidify with HCl and reduce with Zn	AsH_3 evolved	**Lewisite**, primary dichloroarsines

may sometimes be inferred from the color developed by adsorption on colorless silica gel granules. These colors are listed in Table 20.

Adsorption of War Gases on Activated Carbon from Water.[17]—Water suspected of contamination with war gases may be analyzed in the following manner. Shake 1 liter of water with 0.25–0.5 gram of activated charcoal for 0.5 hour in the cold. Filter and dry granules between filter paper. To transfer any gas to silica gel, warm in a glass tube in a slow current of air. The evolved gases are adsorbed on the silica gel further along in the tube. In general, 5 to 10 mg. of gas per liter can be detected by this procedure.

Phosgene and diphosgene cannot be detected because they are hydrolyzed. Mustard gas is partially hydrolyzed but may at times be detected. Diphenylaminechloroarsine will give its test with sulfuric acid, see page 129, directly on the charcoal with the production of a red color after about 5 minutes, if about 2 mg. per liter is present.

TABLE 20

COLORS DEVELOPED BY ADSORPTION ON SILICA GEL

SUBSTANCE	COLOR
Chlorine	Yellow-green
Bromine	Brown
Phosgene	Canary-yellow
Diphosgene	Canary-yellow
Mustard gas	Light yellow
Methyldichloroarsine	Yellow-green
Ethyldichloroarsine	Yellow-green
Lewisite	Light yellow
Diphenylaminechloroarsine	Green
(in small quantities)	Blue-green

b) *Analysis of Alcoholic Extract*

This analysis is made principally to detect the presence of persistent lachrymators. Extract a suitable sample by maceration for several minutes with hot absolute alcohol. Filter the alcoholic extract and examine according to the scheme outlined in Table 21.

Sodium Sulfide Precipitate.—If the original alcoholic extract contains an appreciable amount of chemical agent, add 20 per cent aqueous alcoholic sodium sulfide solution, warm, if necessary to induce the reaction, cool, dilute with water, filter off the precipitated sulfide and determine the melting point of compound. Table 22 gives the melting points of compounds formed with some chemical agents. Xylyl bromide gives a mixture of products and ethyliodoacetate gives an oily sulfide which boils at 267° C. Lewisite and other arsenicals also give corresponding sulfides. Chloropicrin yields sulfur and tar.

The alcoholic extract may contain the hydrolysis products of chemical agents, both war gases and screening smokes. Alcoholic extraction will not, in general remove the decomposition products of screening smokes and, if the presence of the latter is suspected, the extracted residue should be boiled with alkali and the filtered solution tested in the usual way for tin, silicon and titanium.

c) *Analysis by Determination of Elements*

If the chemical agent cannot be identified by the methods indicated in the previous sections, it is necessary to attempt to identify it by determining the elements it contains. For this purpose, the gas must first be removed from the contaminated material, either by extraction with dry ether or benzene as explained below, or by volatilization and adsorption on activated charcoal. In the latter method, a modification of the air-flow procedure previously described on page 80 is used. Air, purified by passage over activated charcoal granules and dried by passage over calcium chloride is passed over or through a small quantity of the sample in a glass

TABLE 21

ANALYSIS OF ALCOHOLIC EXTRACTS

PROCEDURE	RESULT	INDICATION
Add alcoholic KOH, warm to hydrolyze	Intense red color resinous products	Chloro or bromoacetone
Filter, if necessary and test portions of the filtrate		
(1) Acidify and test as in Table 18, page 81		
(2) Boil	NH_3 evolved	**Bromobenzyl cyanide, cyanogen halide**
(3) Remove alcohol and oxidize residue with alkaline permanganate, see page 108	Benzoic acid formed	**Benzyl bromide, bromobenzyl cyanide, chloroacetophenone**
(4) Acidify with HAc and test for glycollic acid, page 105		**Ethyliodo** or **bromoacetate**

tube or gas washing bottle maintained at 50° C. by means of a water bath and is then drawn through activated charcoal at a rate up to 0.5 liter per minute for a period of one hour. The activated charcoal used for the adsorption of the chemical agent must be in the form of granules or small cylinders. Suitable portions of these are used for the tests. Use small or micro test tubes for the performance of all tube tests.

Prepare extracts from contaminated soil samples, clothing etc. with the aid of volatile solvents such as anhydrous benzene or ether. The solvents should be anhydrous so that the extraction of impurities from the soil will be avoided and contain no chlorine, which would interfere with the tests. Free the extracts from ether or benzene by the use of a steam bath at gentle heat and the aid of a current of air. All of these operations should be carried out in a fume hood with a good draft and a gas mask should be worn if necessary.

Boiling Point Determinations.—When sufficient extract is available, heat 0.2–0.5 ml. with a few granules of pumice, and suspend a thermometer in the vapors about 2 cm. above the surface of the liquid. It should be noted that rapid heating above the boiling point may cause an explosion with chloropicrin. A trial test should be made on a separate drop of the liquid by observing its behavior on boiling.

TABLE 22

MELTING POINTS OF SULFIDES

SULFIDE	CHEMICAL AGENT
22′-Diketo dipropyl sulfide, m. p. 47° C.	Chloro or bromoacetone
Dibenzyl sulfide, m. p. 49° C.	**Benzyl bromide**
22′-Diketo 33′-diphenyl diethyl sulfide, m. p. 77° C.	**Chloroacetophenone**
Dithian, m. p. 111° C.	**Mustard gas (Dichloroethyl sulfide)**
$\alpha\alpha'$-Dicyanodibenzyl sulfide, m. p. 150° C.	**Bromobenzyl cyanide**

Iron carbonyl decomposes with the formation of an iron mirror and the evolution of a brown smoke of iron oxide. Arsine derivatives in the form of diphenylchloroarsine or diphenylaminechloroarsine give a mirror of arsenic. The boiling and melting points of the poison gases are given in the sections relating to the individual substances, Chapter II and Appendix Table II.

Decomposability in Water.—Heat a capillary drop of the extract with 0.5 ml. of water and test for chloride ions with a 5 per cent solution of silver nitrate.

The following gases or vapors give rise to a halogen acid on contact with water, and so may be detected with an indicator, such as methyl red:—Chlorine, phosgene, diphosgene, benzyl or xylyl bromide (slowly), diphenylchloroarsine, diphenylaminechloroarsine (slowly), methyl and ethyldichloroarsine, chlorovinyldichloroarsine, dichloroethyl sulfide (slowly), methyl and ethyl chlorosulfonate, chloromethylchloroformate, methylchloroformate (with hot water).

Chloropicrin does not decompose and some difficulty may be experienced with the arsines.

Detection of Halogen.—(a) For small quantities of chemical agent of the order of 2 mg. Beilstein's method modified by Dijkstra[18, 19] may be used. Fasten a piece of copper oxide on the end of a copper wire. Moisten the oxide with alcohol and heat to glowing in the oxidizing flame of a gas burner. Repeat until the flame is no longer green. Place a granule of the activated charcoal containing the adsorbed chemical agent in a tube bent as shown in Fig. 6. Heat the tube containing the charcoal and blow air through it, placing the end of the tube under the glowing copper oxide in the flame. The heat of the flame will drive the adsorbed gas from the carbon. The presence of a halogen will be demonstrated by the production of a green flame. Cyanides may also give a positive response to this test.[19]

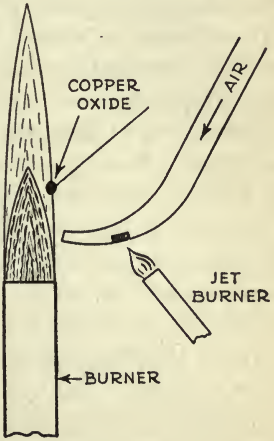

Fig. 6. Dijkstra's Arrangement of Beilstein's Test for Halides

A modification of this test has been suggested by Hayman.[20] Heat a section of Monel metal tubing 0.9 cm. (0.375 inch) in outer diameter to a cherry red color with a Bunsen burner equipped with a fishtail. Place the material to be tested within 1 cm. of the under side of the Monel tube. The material decomposes in the flame and the decomposition products are automatically swept up against the hot metal. If the compound contains halogen, a colored flare will appear which may range anywhere between green and blue. Cyanides do not color the flame if the test is performed this way.

Other modifications of the Beilstein flame test are given on page 77.

(b) Detection of halogens, principally chlorine, in aliphatic compounds and in the side chain of aromatic compounds like chloroacetophenone.—

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[18] Dijkstra, *Chem. Weekblad*, **34**, 351 (1937).

[19] Hoogeveen, *Chemistry & Industry*, **59**, 550 (1940).

[20] Hayman, *Ind. Eng. Chem., Anal. Ed.*, **11**, 470 (1939).

Boil 1 drop of the extract with 0.5–1.0 ml. of a 2 *N* solution of caustic soda in methyl alcohol prepared by dissolving about 5 grams of sodium in 90 ml. of methyl alcohol and diluting to 100 ml. with water. Add 10 per cent nitric acid solution and 5 per cent silver nitrate solution to detect the presence of halide ion.

An alternative method for the detection of halide ion in compounds which do not react quickly to form an acid with water is to pass them into an alcoholic potassium hydroxide solution, with subsequent decomposition and the formation of an alkali halide. The following substances are decomposed by this treatment: Ethylbromoacetate, ethyliodoacetate, bromobenzyl cyanide, bromoacetone, chloro- and bromoacetophenone, phenylcarbylamine chloride, chloropicrin (reacts only slowly), and diphenylchloroarsine.

Detection of Chloride, Sulfate and Arsenic.—Pringsheim's test.—Add about 50–100 mg., equivalent to about 1 to 2 drops of extract, to 0.2 gram of sodium hydroxide and mix with 0.2 gram of sodium peroxide in a nickel crucible. Cover with a lid having a central hole, and ignite the mass with a glowing nickel wire. Dissolve the melt in water and filter. In the presence of iron carbonyl, a residue of ferric oxide will be obtained.

Acidify one-half the filtrate with 10 per cent nitric acid solution and test for chloride or halide ion with 5 per cent silver nitrate solution and for sulfate ion with 5 per cent barium nitrate solution.

Acidify the other half with 20 per cent arsenic-free sulfuric acid. Add zinc and if necessary 1 drop of 1 per cent cupric sulfate solution to cause hydrogen evolution. Any arsine formed is detected with moist mercuric chloride test paper by the formation of a yellowish coloration. The mercuric chloride test paper is prepared by moistening with 7 per cent mercuric chloride solution or by impregnating with 5 per cent alcoholic mercuric chloride solution and permitting the paper to dry in air. Preferably a Gutzeit test or molybdenum blue test should be performed as directed in Chapter V, page 92 and sequence.

Detection of Nitrogen.—(a) *Micro method.*—Heat the charcoal granule containing the chemical agent in a tube in order to oxidize it and blow out the oxidized gas into a drop of concentrated sulfuric acid in a small test tube. Add a crystal of diphenylamine. If nitrogen is present, a blue coloration showing the presence of nitrates or nitrites is obtained on the addition of hydrochloric acid. Carry out a blank test for the reaction occurs with a various oxidizing agents and is not specific for nitrates. As an alternative procedure, add a little ferrous sulfate to the acid test solution. A brown color indicates the presence of nitrogen peroxide. This reaction is not as sensitive as the diphenylamine test but is more specific.

(b) *Macro method.*—Test for cyanide.—Heat carefully two drops of the substance or of the concentrated ethereal extract with metallic sodium in a test tube and then plunge the hot tube into 3 ml. of water. Heat half the solution with a small lump of ferrous sulfate and acidify with hydrochloric acid. A blue coloration (Prussian blue) indicates the presence of nitrogen. Chloropicrin, diphenylcyanoarsine and dichloroformoxime respond to this reaction. Test the remaining half of the solution for sulfur as directed below. Cyanide may also be detected by the benzidine copper acetate test described on page 119. Prepare the test paper as detailed and hold it above the liquid in the tube containing the acid test solution. A blue color shows the presence of cyanide and thus of nitrogen.

If an ethereal extract is used for the test, a blank determination should also be carried out on a similar substance known to be uncontaminated, in order to avoid any possibility of error due to the presence of soluble nitrogen compounds in the foodstuff or other material itself. In some cases it is useless to carry out this test, since the extract is certain to contain nitrogen compounds; for example, from coffee or tea, caffeine would readily be extracted by benzene. Air-flow analysis may help at times. It is assumed, of course, that sufficient carbon will be present in the ethereal or benzene extract to give the cyanide reaction. Cyanide may itself be present as the chemical agent, and a direct test on air drawn over the foodstuff may therefore be used in addition.

Detection of Sulfur.—(a) *Micro method.*—Moisten the granule of activated charcoal containing the gas with sodium hydroxide solution and heat with sodium in a small combustion tube. After ignition, break the tube so that the contents fall into a little water placed on a silver coin. If sulfide is present a stain of black silver sulfide will be produced. A blank test should be carried out on some of the uncontaminated material. (b) *Macro method.*—Filter the remaining half of the solution used for test for nitrogen by the macro method, above. Add 2 drops of 10 per cent sodium nitroprusside solution, 10 grams of $Na_2Fe(CN)_5NO.2H_2O$ dissolved in water and made up to 100 ml. In the presence of sulfide, a violet coloration appears. Mustard gas responds to this test.

Detection of Arsenic.—Proceed as described in Chapter V page 89.

Other Group Reactions.—The following give hydrogen cyanide on hydrolysis with water, and may be detected by the Prussian blue reaction: Hydrogen cyanide, (possibly mixed with stannic salts), cyanogen chloride, (slowly hydrolyzed in water, quickly by alkali), diphenylcyanoarsine and diphenylaminecyanoarsine.

The following give an arsenic reaction when absorbed in alkaline permanganate solution: Diphenylchloroarsine, diphenylcyanoarsine, diphenylaminechloroarsine, diphenylaminecyanoarsine, chlorovinyldichloroarsine and ethyldichloroarsine.

The following will give colors with concentrated sulfuric acid: Diphenylaminechloroarsine, in the cold, a red coloration; bromobenzyl cyanide, warmed, a red coloration.

V. DETECTION AND DETERMINATION OF ARSENIC

The detection and estimation of arsenic is one of the most important of all analyses to be performed by the civilian defense war gas chemist, particularly in food products suspected of contamination with arsenicals. This is not, of course, to minimize the detection and identification of vesicants like mustard gas. Because of arsenic's prominent and dangerous position among war gas elements and because it is difficult at times to ascertain the true amount of arsenic present, special consideration must be given to the methods for its detection and determination.

I. Tolerance

The amount of arsenic which may be permitted or tolerated in a food if the food is to be considered wholesome is debatable. The tolerance established for arsenic in foods is 1.4 parts per million or 0.01 grain per pound. However, in the case of spray residue, that is the insecticide remaining on fruit after commercial washing, this tolerance has been increased to to 3.58 parts per million or 0.025 grain per pound.

There are two principal reasons why the tolerance for arsenic in foods polluted with arsenical war gases should be at least as strict as 1.4 parts per million. First, no washing of most foodstuffs will ordinarily be done as in the case of spray residue on fruits; hence foods contaminated with war gases should be placed in the regular category. Second, the arsenical war gas may be harmful not only because it is an internal poison due to the arsenic it contains, but also because the war gas, per se, is a harmful substance or gives rise to harmful substances. Thus, if Lewisite impinges on a foodstuff by which it is hydrolyzed, the hydrolytic product, chlorovinylarsenious oxide, is a vesicant solid.

II. Acid Digestion

Because most of the arsenic bearing war gases are organic compounds and many of the polluted materials are organic compounds some description of the customary methods for the destruction of organic matter is appropriate at this point. There are two general methods for the destruction of interfering organic matter. The first is called the "wet ash" or acid digestion method and the second is ordinary ashing by means of heat with, or without, the aid of an "ash aid" mixture or of an alkaline fixitive for volatile metals, such as arsenic, antimony, mercury or tin. Acid digestion is to be preferred for these metals except in the instance of antimony.

Transfer the sample or an appropriate aliquot or portion containing the arsenic to an 800 ml. Pyrex Kjeldahl flask. If the sample is a liquid and an oxidizing medium is present so that no arsenic will be lost on evaporation, the sample may be concentrated by evaporation. Add 50 ml. of concentrated nitric acid and then carefully add 20 ml. of concentrated sulfuric acid. Heat cautiously so that no excessive foaming takes place. Add nitric acid in small portions until all the organic matter is destroyed. This point is reached when no further darkening of the solution occurs on continued heating after the production of a clear solution and copious fumes of sulfur trioxide. Cool, add 75 ml. of water and 25 ml. of a saturated solution of ammonium oxalate to aid in the expulsion of nitrogen fumes. Evaporate again to the appearance of sulfur trioxide fumes. Cool, dilute with water, transfer to a 500 ml. or liter volumetric flask, and make to volume. Use aliquot portions for analysis as needed.

Wet ashing by means of nitric acid and potassium permanganate and by means of sulfuric acid and potassium permanganate has been described in the literature in connection with methods for the estimation of mercury. In recent years methods of ashing by means of nitric and perchloric acids[1, 2, 3] have been developed in order to overcome the difficulties presented by substances volatile or having an appreciable vapor pressure at the boiling temperature of a mixture of nitric and sulfuric acids, or which produce an insoluble precipitate in those acids. The author finds it difficult to recommend these procedures, for ashing with perchloric acid is extremely dangerous, serious explosions having occurred during its use. All the details may be found in the chemical literature.

III. Detection

1. REINSCH TEST

The Reinsch test is a simple though not very sensitive one. It is based on the deposition of arsenic from solution as a copper arsenide. The test may very often be applied directly without previous destruction of organic matter. Place 200 ml. of the suspected arsenic bearing material, if trapped in water by an impinger or a bubbler device, in a casserole, or place some of the sample in a casserole and dilute to 200 ml. Acidify with 1 ml. of arsenic free hydrochloric acid. Evaporate to one-half its volume. Add 15 ml. more of hydrochloric acid and also a piece of pure burnished

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[1] Gieseking, Snider and Getz, *Ind. Eng. Chem., Anal. Ed.*, 7, 185 (1935).

[2] Gerritz, *Ind. Eng. Chem., Anal. Ed.*, 7, 167 (1935).

[3] Jacobs, *Chemical Analysis of Foods and Food Products*, Van Nostrand, New York, 1938.

copper foil. Keep the liquid simmering for an hour and replenish the water lost by evaporation from time to time. If at the end of this time the copper foil remains bright, arsenic is absent in greater quantity than traces. If the copper has a black or brown deposit, remove it and wash well with water, alcohol, and ether, and dry. Place the foil in a subliming tube and heat over a low flame. If a sublimate is present, examine it under a microscope. Arsenic forms tetrahedral crystals in contradistinction to mercury which forms globules. Antimony, silver and bismuth will also give a deposit on the copper foil but will not sublime with the application of heat.

2. BETTENDORFF TEST

The Bettendorff test is based on the observation that stannous chloride solution will reduce arsenic compounds to the metallic state in the presence of concentrated hydrochloric acid.

Boil the sample with 2 ml. of 30 per cent sodium hydroxide solution until the volume of the test solution is halved. Cool, neutralize cautiously with concentrated hydrochloric acid. Add several ml. of concentrated hydrochloric acid in excess. Cool and filter, if necessary, into a dry test tube. Add 2 ml. of a 33 per cent solution of stannous chloride in concentrated hydrochloric acid. The development of a yellow or brown color or precipitate of free arsenic can be accelerated by gentle warming or by the addition of 1 drop of 0.25 per cent solution of mercuric chloride in concentrated hydrochloric acid.

3. HOFFMANN TEST

A relatively simple test which can at times be applied without an acid digestion of the sample is the Hoffmann test. In this test arsine is evolved and is trapped in silver nitrate solution. The formation of metallic silver is an indication of arsenic.

$$AsH_3 + 6AgNO_3 + 2H_2O \rightleftarrows 6Ag + HAsO_2 + 6HNO_3$$

Place some of the sample in a test tube with a bulb bottom. Equip the test tube with a bent tube adapter having a jet at its end so that it can be immersed in a few ml. of 2.0 per cent silver nitrate solution. Add some granulated zinc and dilute hydrochloric acid to the sample, stopper the tube with the cork holding the adapter, and allow the evolution of arsine to proceed. A dark coloration or black precipitate beginning at the jet and extending through the solution is evidence of the presence of arsenic or antimony. The use of a wad of absorbent cotton wet with lead acetate solution placed in the end of adapter in the test tube will prevent any hydrogen sulfide from passing into the silver nitrate solution. The addition of potassium iodide solution and stannous chloride-hydrochloric acid solution (see below) may assist the evolution of arsine.

Antimony evolved as stibine also gives a black precipitate with silver nitrate solution but this precipitate is silver antimonide Ag_3Sb.

IV. Determination

1. GUTZEIT METHOD[4]

The Gutzeit method is based on the liberation of arsine under carefully controlled conditions from an arsenic solution. The arsine subsequently reduces mercuric bromide on a prepared strip of paper with the production of stains. The stain, if the method is followed in detail, is proportional to the amount of arsenic present.

Prepare a generator, as follows: Use a 2 ounce wide mouth bottle. Equip the bottle by means of a perforated stopper with a glass tube 1 cm. in diameter and 6–7 cm. long, with an additional constricted end to facilitate connection. Place a small wad of glass wool in the constricted bottom end of the tube and add 3.5 to 4 grams of 30-mesh clean sand. Moisten the sand with 10 per cent lead acetate solution and remove the excess by light suction. The lead acetate is used to remove any hydrogen sulfide that might be generated along with the arsine and thus vitiate results, if permitted to reduce the mercuric bromide. Connect the tube by means of a rubber stopper with a narrow glass tube 2.6–2.7 mm. in internal diameter, and 10–12 cm. long, and place in this tube a strip of mercuric bromide paper. These strips may be made by cutting paper similar to Whatman No. 40 filter paper, into strips exactly 2.5 mm. wide and about 12 cm. long. Commercial strips are available. Soak the strips for 1 hour or longer in a fresh 3–6 per cent solution of mercuric bromide in 95 per cent alcohol. Dry and use within 2 days. For approximately quantitative work, these strips may be stored in a well-stoppered blackened tube.

Determine the acid in an aliquot of the solution prepared from the wet ash as described above. Place aliquots not to exceed 30 ml. depending on the amount or arsenic trioxide, 0.01 to 0.03 mg., in the Gutzeit generator. If the aliquot contains only hydrochloric acid, add sufficient hydrochloric acid to make a total volume of 5 ml. If it contains sulfuric acid, add sufficient 25 per cent, arsenic free sodium hydroxide to exactly neutralize it and add 5 ml. of hydrochloric acid; or add sufficient hydrochloric acid to the sulfuric acid in the aliquot to make a total volume of 5 ml. Cool, if necessary, and add 5 ml. of potassium iodide solution, 15 grams of potassium iodide dissolved in water and made up to 100 ml., and 4 drops of stannous chloride solution, 40 grams of arsenic free stannous chloride, $SnCl_2.2H_2O$, in hydrochloric acid made up to 100 ml. with hydrochloric

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[4] *Methods Assoc. Official Agr. Chemists* (5th ed.) 1940.

acid. Add a piece of activated zinc, 10 to 15 grams in weight or 2 to 5 grams of granulated zinc, center the strip of mercuric bromide paper in its tube, and set the tubes in position.

Immerse the apparatus in a water bath kept at 20–25° C. to within 1 inch of the top of the narrow tube and allow the evolution of the arsine to proceed for 1 hour or one and one-half hours. Remove the strip and average the length of the stains on both sides in mm. Locate the length of the unknown on a standard graph and read off on the abscissas the quantity of arsenic present. The graph may be made by running known quantities of arsenic by the above method using length of stain as ordinates and mg. of arsenic trioxide as abscissa. Many authorities advise against the use of a standard graph on the ground that one cannot be prepared. They advise the running of a series of controls with every unknown determination.

All the reagents used in this determination should be arsenic free. However, as a precaution, it is best to run blanks on the reagents. In some cases the test may be made without previous destruction of organic material but the results obtained are probably only approximate. An aliquot containing 0.02 to 0.025 mg. of arsenic trioxide is considered optimum for reading the stain.

2. COPPER SULFATE DIGESTION METHOD[5]

The usual acid digestion is not always adequate for the decomposition of arsenical war gases. In particular, diphenylchloroarsine, DA, and similar toxic smokes, are difficult to detect. The following method in which the digestion is performed with the aid of sulfuric acid, potassium sulfate and copper sulfate, acting as a catalyst, is designed to overcome this difficulty.

Digest a suitable quantity of the thoroughly mixed sample with 10 grams of potassium sulfate, 2 ml. of copper sulfate solution, 10 grams of $CuSO_4.5H_2O$ dissolved in water and diluted to 100 ml., and 20 ml. of arsenic free sulfuric acid, or with sufficient sulfuric acid to allow 8 ml. for every gram of dry material in the portion taken for analysis. When the sample contains a high proportion of fat or oil, it may be necessary to add a further 5 to 10 ml. of sulfuric acid during the digestion. When clear, dilute the liquid with about 70 ml. of water and boil for 2 to 3 minutes, until free from any odor of sulfur dioxide. Cool, transfer to a volumetric flask and dilute to 100 ml. with water.

Take suitable aliquot portions for Gutzeit tests and dilute to 50 ml. with a solution containing 10 per cent of potassium sulfate, 0.2 per cent of copper sulfate and sulfuric acid (1:9). Variations in the strength of the

[5] Williams, *Analyst*, **66**, 228 (1941).

residual sulfuric acid caused by the different types of food digested do not appear to affect the stains in the Gutzeit test but it may be advisable to determine the amount of residual acid and adjust to constant acidity as is done in the A.O.A.C. method for each test.

After the addition of 0.5 ml. of stannous chloride solution, carry out the Gutzeit test, page 92. Prepare standard stains for comparison under similar conditions, with 50 ml. of the diluting solution and 0.5 ml. of stannous chloride solution for each, taking care to see that the contents of the tube are in a similar state of humidity, for both excessive moisture and excessive dryness appear to cause weak stains.

3. RAPID METHOD FOR THE DETERMINATION OF LEWISITE[6]

If preliminary tests show that Lewisite is the contaminating agent, a rapid Gutzeit may be run to estimate the amount of arsenic present. In this method, Lewisite is decomposed with sodium hydroxide solution. The arsenic is reduced to the arsenious state by the use of stannous chloride and potassium iodide. Arsine is generated in the usual manner with zinc and hydrochloric acid, and is estimated by a Gutzeit test.

Weigh 1 gram of the material to be examined into a Pyrex tube, 6 inches by 1 inch, and add 10 ml. of a sodium hydroxide solution, 20 grams of NaOH dissolved in water and made up to 100 ml. Heat the mixture to boiling over a small flame with constant shaking and then boil very gently for 5 minutes in such a manner that no serious diminution in volume occurs. Transfer the residue to a 4 ounce wide mouth bottle, rinsing out the tube with two successive 5 ml. portions of water. Add 20 ml. of freshly prepared stannous chloride solution, 40 grams of $SnCl_2.2H_2O$ dissolved in concentrated hydrochloric acid and made up to 100 ml. with this acid. Mix well by vigorous swirling. Add 1 ml. of a freshly prepared solution of potassium iodide, 10 grams of KI in 100 ml. of water, and mix. Allow the mixture to stand for half-an-hour. Add 20 ml. of 15 per cent sulfuric acid, followed by 10 grams of zinc. Do not use excessively large pieces of zinc. Activate the zinc immediately before use by immersion for three minutes in a mixture of 1 part of concentrated hydrochloric acid and 2 parts of water, using 2 ml. of this mixture for each gram of zinc. Decant the acid, and wash the zinc twice by decantation with hot water.

Close the bottle with the rubber stopper carrying the Gutzeit tubes and complete the estimation in the normal manner except to allow the reaction to proceed for 1.5 to 2 hours, 20 minutes at room temperature and the remainder of the time in a water bath at 35–40° C. Amyl alcohol may be added, if necessary, to prevent excessive frothing.

Prepare the standard stains by adding standard arsenic solution to a

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[6] Stainsby and Taylor, *Analyst*, **66**, 233 (1941).

previously cooled mixture of 10 ml. of the 20 per cent sodium hydroxide solution, 10 ml. of water and 20 ml. of stannous chloride solution prepared as directed above, completing the procedure in the same manner as for the samples. A blank determination should be carried out on the reagents, bearing in mind the possibility that the tubes employed may yield soluble arsenic during the alkali treatment.

4. GUTZEIT-MOLYBDENUM BLUE METHOD

The molybdenum blue method for the estimation of arsenic is one of the most sensitive methods that can be used for this purpose. Phosphorus reacts with ammonium molybdate to form a complex molybdiphosphate. This may subsequently be reduced with the formation of a complex molybdenum compound strongly colored blue. Arsenic undergoes an entirely analogous reaction with the formation of an intensely colored blue complex.

The arsenic is put into solution by methods previously detailed. It is evolved as arsine, which is trapped and oxidized by sodium hypobromite solution. Ammonium molybdate is added, and the color of molybdenum blue is developed by the use of hydrazine sulfate, $N_2H_4 . H_2SO_4$.

Apparatus.—The apparatus used consists of the official Gutzeit generator, page 92 and a trapping device similar to that used for the determination of benzene or toluene in air by the butanone method.[7, 8] This arrangement is illustrated in Fig. 7. If the benzene trap is not available, a simple trap can be made by bending a 17.6 ml. or 20 ml. pipette into the form of the trap shown in the illustration and then filling the bulb portion with beads. The tube containing the mercuric bromide test paper in the usual Gutzeit method is replaced by another tube leading the generated gases to the trapping device.

Preparation of Sample.—Make an acid digestion or use the solvent procedure of Wichmann and Clifford as detailed in the methods of the Association of Official Agricultural Chemists[9] or by Jacobs,[10] or, if necessary, employ combustion methods. Then prepare an aliquot for an official Gutzeit test as directed in the aforementioned texts. From this point proceed as directed in the following method.

Reagents.—1) Sodium hypobromite solution.—Add 0.5 *N* sodium hydroxide solution to half-saturated bromine water in the proportion of 1 ml. of 0.5 *N* sodium hydroxide solution to every 3 ml. of bromine water.

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[7] Schrenk, Pearce and Yant, *U. S. Bur. Mines Repts. Investigations*, **3287** (1935).

[8] Jacobs, *The Analytical Chemistry of Industrial Poisons, Hazards and Solvents.* Interscience, New York, 1941.

[9] *Methods Assoc. Official Agr. Chemists* (5th ed.) 1940.

[10] Jacobs, *The Chemical Analysis of Foods and Food Products*, Van Nostrand, New York, 1938.

2) Saturated bromine water.—Add 2 ml. of liquid bromine to 200 ml. of water in a 250 ml. glass stoppered bottle. Shake well and allow to stand. Dilute with an equal volume of water before use in the preparation of the sodium hypobromite solution.

3) Ammonium molybdate solution.—Dissolve 25 grams of ammonium molybdate in 300 ml. of water. Dilute 75 ml. of concentrated sulfuric acid to 200 ml. with water and add to the ammonium molybdate solution.

4) Standard arsenious oxide solution.—Dissolve 0.300 gram of arsenic trioxide, As_2O_3, in 25 ml. of 10 per cent sodium hydroxide solution, made slightly acid with sulfuric acid (1:6), and dilute with water to 1 liter. Dilute this stock solution, which may be standardized against standard potassium bromate solution, if desired, to an appropriate dilution to make for ease in the removal of aliquots to be used for the standards in the development of the color. Thus, for example, a 5 ml. aliquot of the stock standard solution diluted to 1 liter yields a solution 1 ml. of which is equivalent to 1.5 micrograms of arsenic trioxide. This dilute standard should be prepared fresh from the stock standard solution.

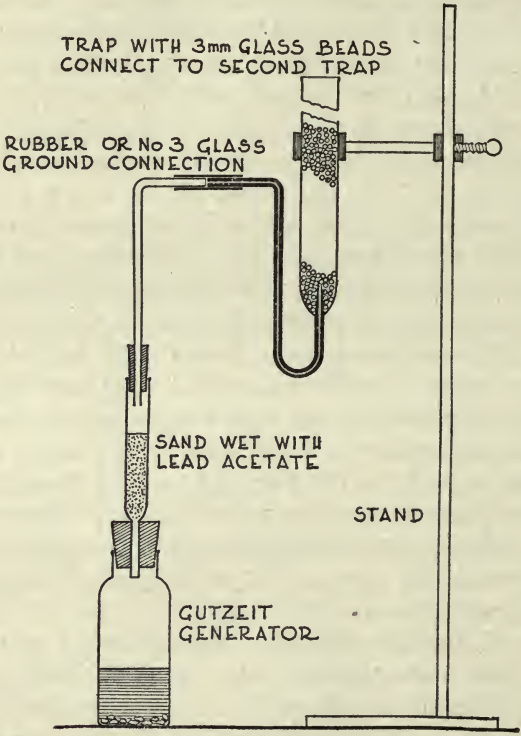

FIG. 7. Apparatus for the Gutzeit-Molybdenum Blue Method

5) Hydrazine sulfate solution.—Prepare a saturated solution of hydrazine sulfate, $N_2H_4 . H_2SO_4$. Dilute an aliquot of the supernatant liquid 1:1 with water.

6) Sulfuric acid.—Prepare a 2 N solution of sulfuric acid and standardize against standard alkali in the usual manner.

Procedure.—Allow the generation of arsine to proceed as directed in the Gutzeit method and trap the arsine in the bead device to which 3 ml. of sodium hypobromite solution has been added. After generation is completed, that is, after an hour to hour and a half, transfer the contents of the trap to a graduated colorimeter tube, Nessler tube or volumetric flask. Wash the trap with six 2 ml. portions of distilled water delivering the water to the trapping device with a 2 ml. pipette. Use a rubber bulb aspirator to blow the wash solutions out of the trap into the collection vessel. Press the aspirator bulb gently in this step. Add exactly 5 ml. of 2 N sulfuric acid and stir. Add 1 ml. of ammonium molybdate reagent and shake. Add 1 ml. of the half-saturated hydrazine sulfate solution and swirl. Make to a volume of 25 ml. Allow to stand for 0.5 hour for full development of the blue color. Compare with standards or a standard treated in a similar way at the same time.

Preparation of Standards.—The standards or standard are prepared from the diluted stock standard arsenious oxide solution. Add 3 ml. of sodium hypobromite solution to the aliquot or aliquots selected. Dilute to 15 ml. with distilled water. Add exactly 5 ml. of 2 N sulfuric acid and stir. Add 1 ml. of the molybdate reagent, stir, add 1 ml. of half-saturated hydrazine sulfate solution and stir. Make up to the same volume as the test solution. A blank should be run on all the reagents as a check.

It is important to note that if a final volume of 25 ml. is to be used in making the comparisons, exactly 5 ml. of 2 N sulfuric acid should be used in order to have the proper acidity for the development of the molybdenum blue color. If less than this quantity of acid is used, the blank may itself be reduced. If more than this quantity of acid is used, the development of the blue complex will be delayed.

5. FIELD TEST

The person making the test should be suitably masked and clothed with protective devices.

Attach a glass funnel to the bead trap containing the 3 ml. of sodium hypobromite solution described in the arsine-molybdenum method. Connect the trap, in turn, to a rubber bulb aspirator or similar device arranged for suction. Hold the funnel over the spot to be tested, or in the air which is to be examined, or fill the funnel with the material to be analyzed. Draw air through the alkali hypobromite solution by alternate compressions and releases of the rubber bulb. An approximate idea of the volume of air sampled may be obtained from the number of compressions of the rubber bulb aspirator and the capacity of the rubber bulb. After sampling is complete, detach the funnel and the aspirator bulb from the trap. Transfer the contents of the trap to a tube and proceed with the method as outlined, omitting washing the trap if desired; nor is it necessary to wait full time for color development.

Phosphates, if present, may interfere. This, however, can be checked by reducing arsenates (trapping the air to be tested in water, instead of in hypobromite solution) with potassium iodide, which will not reduce the phosphate, and then applying the molybdenum blue test. The difference in blue color obtained is a measure of the arsenate present. As little as 1 microgram can be detected. A blue color chart can be made for approximately quantitative results. The amount in the air can be roughly estimated from the volume of air sampled and the blue color developed.

Water may be tested directly without evolution of arsine as if it were a standard.

If desired, the arsine evolution may be performed directly in the field as detailed for the Hoffmann test, page 91.

VI. CONFIRMATORY TESTS

GENERAL REFERENCES

Cox, *Analyst*, **64**, 807 (1939).
Hoogeveen, *Chemistry & Industry*, **59**, 550 (1940).
Degand, *J. pharm. Belg.*, **21**, 895 (1939).
Jacobs, *The Analytical Chemistry of Industrial Poisons, Hazards and Solvents.* Interscience, New York, 1941.
Analyst, **66**, 44 (1941).

CLASSIFICATION ACCORDING TO CHEMICAL CONSTITUENTS

On the basis of the elements found by the examination of the gases adsorbed on activated carbon or in the residue from the solvent extraction as described in Chapter IV, page 83 and sequence, chemical warfare agents may be divided into five principal categories. For the purpose of this classification the elements carbon, hydrogen and oxygen are ignored except in Group V.

I. Halogen only.—[Chlorine], [hydrochloric acid], [bromine], [**phosgene**], **diphosgene,** ethylbromoacetate, **ethyliodoacetate,** methylchloroformate, chloromethylchloroformate, bromoacetone, bromomethylethyl ketone, **chloroacetophenone,** benzyl bromide, xylyl bromide, and dichloromethyl ether.

IIa. Sulfur only.—[Hydrogen sulfide], dimethyl sulfate.

IIb. Sulfur and halogen.—**Mustard gas,** thiophosgene, **chlorosulfonic acid,** methylchlorosulfonate, ethylchlorosulfonate, perchloromethyl mercaptan, sulfuryl chloride, thionyl chloride, and sulfur monochloride.

IIIa. Nitrogen only.—[Hydrogen cyanide].

IIIb. Nitrogen and halogen.—Cyanogen chloride, cyanogen bromide, **bromobenzyl cyanide, chloropicrin,** phenylcarbylamine chloride, monochloroformoxime and dichloroformoxime.

IVa. Arsenic only.—[Arsine].

IVb. Arsenic and halogen.—**Lewisite, methyldichloroarsine, ethyldichloroarsine, phenyldichloroarsine,** [**diphenylchloroarsine**], arsenic trichloride.

IVc. Arsenic, halogen and/or nitrogen.—[**Diphenylcyanoarsine**], [**diphenylaminechloroarsine**], and [diphenylaminecyanoarsine].

In addition to the above groups, there is a miscellaneous group in which must be placed:

Va. [Carbon monoxide].

Vb. **Phosphorus** and phosphorus pentoxide.

Vc. Screening smokes like titanium, tin and silicon tetrachlorides.

The chemical agents most likely to be encountered in war are given in bold face type. Those, however, which because of their non-persistent character will seldom be found as material contaminants are enclosed in square brackets.

Group I

1. CHLORINE, Cl_2

a) Test Papers

1. Starch-Iodide Paper.—Bring 75 ml. of water to boiling; mix 1 gram of soluble starch with 10 ml. of water to a paste. Add the paste to the boiling water. Stir vigorously and cool. Add 2 grams of zinc chloride and 2 grams of potassium iodide, stir until dissolved and make up to 100 ml. Impregnate test paper with this solution and allow to dry.

This paper turns blue in the presence of chlorine, bromine and in general, in the presence of oxidizing agents.

2. *o*-Tolidine Paper.—Dissolve 0.1 gram *o*-tolidine in 100 ml. of 10 per cent hydrochloric acid. Immerse filter paper in this solution and hold it in the stream of suspected gas or air or suspend in the suspected atmosphere. Chlorine gives a yellow-orange color.

3. Potassium Bromide-Fluorescein Paper.—Dissolve 0.2 gram of fluorescein, 30 grams of potassium bromide, 0.2 grams of potassium hydroxide, 2 grams of sodium carbonate, and 10 ml. of glycerol in water and make up to 100 ml. Impregnate filter paper with this solution and dry. This paper changes from yellow to red in the presence of chlorine.

4. Mercurochrome Paper.—Dissolve 0.5 gram of mercurochrome, disodium dibromohydroxymercurifluorescein, in 100 ml. of water. Impregnate filter paper and dry in air. Used dry, this paper gives a yellow color with halogens but is not affected by cyanides.

It may be necessary to oxidize a chemical agent with 25 per cent chromic acid or lead dioxide in order to liberate the halogen. Drop a charcoal granule (see Chapter IV) into a test tube containing the oxidizing agent. Cover the mouth of the tube with the test paper and heat gently.

b) Test Solution

Iodide-Thiosulfate Method.—A simple method for the detection and determination of chlorine in air is to pass the air through two bubblers in series, the first containing 4 per cent potassium iodide solution and the second containing a 2 per cent potassium iodide solution. The incoming chlorine reacts with the potassium iodide liberating iodine. Most of this is fixed by the potassium iodide with the formation of triiodide but any iodine carried out in the effluent air is trapped by the second bubbler. The solutions are combined and the free iodine is titrated with 0.1286 *N* sodium thiosulfate solution. One ml. of this solution is equivalent to 1000 parts per million of chlorine by volume at 25° C. and 760 mm. of mercury for a 1 minute sample of 1571 ml.[1]

Quantitative methods for the determination of chlorine in air are described by Jacobs.[2]

2. HYDROCHLORIC ACID, HCl

Hydrochloric acid as well as other chlorides may be detected in air simply by trapping the fumes or dust in a standard solution of sodium hydroxide in an impinger or efficient gas washing bottle. This absorbing solution may then be transferred to a flask and the excess sodium hydroxide determined by titration with standard sulfuric acid, in so far as the acidity is concerned. The amount of chloride may be estimated by the Volhard method. Sodium carbonate solution is also used as the absorbing agent.

Volhard Method.—The thiocyanate method for the determination of chloride in which the silver chloride precipitate is removed by filtration before back-titrating may be improved by eliminating the filtration. This may be done by the use of nitrobenzene[3] which inhibits the darkening of silver chloride in the light and improves the end point. This immiscible liquid draws the silver chloride to the interface and thus removes it from the aqueous solution, the nitrobenzene forming an insoluble layer over the precipitate.

Titrations may be made in 250 ml. glass stoppered bottles. Twenty-five to 50 ml. of the sample solution, free from the usual interfering ions, is acidified with 8 to 10 drops of nitric acid, and 1 ml. of nitrobenzene is added for each 0.05 gram of chloride. Standard silver nitrate is added until an excess of 1 to 4 ml. of 0.1 *N* solution is present. The bottle is then tightly stoppered and shaken vigorously until the silver chloride settles out in large spongy flakes. Usually 30–40 seconds agitation is required. A perfectly clear supernatant solution is not necessary. Fine droplets of nitrobenzene are left in suspension. However, nearly all the nitrobenzene is so closely attached to the silver chloride that there is little evidence of a separate phase.

One ml. of ferric alum indicator, prepared by adding concentrated, freshly boiled nitric acid to a saturated solution of ferric alum until the solution becomes greenish yellow, is added and the titration completed with 0.05 *N* potassium thiocyanate solution. The ferric alum acts as an effective

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[1] Fieldner, Oberfell, Teague and Lawrence, *Ind. Eng. Chem.*, **11**, 523 (1919).

[2] Jacobs, *Analytical Chemistry of Industrial Poisons, Hazards and Solvents*, Interscience, New York, 1941.

[3] Caldwell and Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

flocculating agent and coagulates any suspended matter which is present. Standard potassium thiocyanate solution is added slowly with gentle swirling until a pink color is produced. Usually a false end point appears one drop before the true end point. It fades in about 30 seconds and may be due to the desorption of the last traces of silver nitrate from the precipitate. The next drop of thiocyanate produces a decided color change which persists 10 to 15 minutes. Titration should be made at temperatures below 25° C., as is customary in other titrations with thiocyanate. If nitric acid and subsequent boiling was used in the preparation of the sample, the addition of a saturated solution of hydrazine sulfate just prior to the addition of the ferric alum indicator, removes any nitrous acid formed.

A refinement of the method of trapping the hydrochloric acid fumes is to draw 20 to 50 liters of air through a solution of glycerol-potassium carbonate-water in the ratio of 1:1:1 in a gas washing bottle.[4] The chloride concentration may then be determined by the Volhard method or by the modification of the Volhard method detailed above.

3. BROMINE, Br_2

a) Test Papers

1. Fluorescein Paper.—Dissolve 10 mg. of fluorescein in 100 ml. of an alcohol-water (1:1) mixture to which a few drops of sodium hydroxide solution have been added. When used damp, this paper gives a rose color with bromine. It is not affected by chlorine.[5]

2. Fuchsin-Sulfurous Acid Paper.—Dissolve 0.1 gram of fuchsin in 100 ml. of water. Add a 5 per cent solution of sodium bisulfite dropwise until just decolorized. This test paper used damp and freshly prepared gives a violet color with bromine vapor. It is not affected by chlorine.[5]

b) Test Solution

A simple method for the detection and estimation of bromine and inorganic bromides is to pass the air through a gas washing bottle containing a cold solution of potassium hydroxide:

$$Br_2 + 2KOH \rightarrow KBr + KBrO + H_2O$$

Add some hydrogen peroxide to react with the hypobromite:

$$KBrO + H_2O_2 \rightarrow KBr + H_2O + O_2$$

and then estimate the bromide as silver bromide.

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[4] Heller, *Gesundh.-Ing.*, **55**, 261 (1932).

[5] Hoogeveen, *Chemistry & Industry*, **59**, 550 (1940).

4. PHOSGENE, $COCl_2$

a) *Test Papers*

1. Harrison's Reagent.—The yellow or orange stain produced by phosgene on test paper containing *p*-dimethylaminobenzaldehyde and diphenylamine has been adopted as the standard test for the detection of phosgene in Great Britain. Dissolve 5 grams of *p*-dimethylaminobenzaldehyde and 5 grams of diphenylamine in 100 ml. of alcohol. Moisten filter paper with this reagent. Dry in a current of carbon dioxide. Alternatively the reagent may be prepared by dissolving 5 grams of each substance in 50 ml. of carbon tetrachloride. Papers prepared by impregnation with the latter solution do not need to be dried in a stream of carbon dioxide. These papers are sensitive to light and should be stored in a blackened tube.

A yellow or orange stain indicates phosgene. Chloromethylchloroformate (palite) and diphosgene give the same reaction.

The stains produced by phosgene are transient, and the test papers are sensitive to chlorine and hydrogen chloride which cause an orange-yellow color. To remove traces of these gases, the atmosphere to be tested is drawn through a guard tube containing pumice impregnated with sodium thiosulfate before it comes in contact with the test paper.

The test, which is capable of detecting less than 1 part per million, may be made quantitative by drawing known volumes of the air to be tested through a definite area of the test paper by means of a suction hand pump of known capacity as described on page 67, and noting the number of strokes required to produce stains of certain intensity. The concentration is then obtained by reference to standard stains on a color chart.

Patty[6] states that this phosgene test paper method is more reliable and satisfactory than any other published method for the estimation of phosgene in concentrations of 0.5 to 2 parts per million. When the paper is suspended in the atmosphere, 0.5 part per million phosgene produces a light lemon yellow color in 4–5 minutes and a dark yellow in 10–15 minutes. Higher concentrations produce proportionately greater color changes up to a dark orange shade which occurs in about 8 minutes for 2 parts per million; and 15 minutes with 1 part per million.

2. Nitrosodimethylaminophenol-Diethylaminophenol Paper.—A reagent filter paper is prepared by soaking it in a mixture of 5 ml. of 0.5 per cent solution of 1,3,6-nitrosodimethylaminophenol and 2 ml. of a 0.5 per cent solution of *m*-diethylaminophenol, both in xylene. This paper held in the suspected atmosphere gives a green color with traces of phosgene. If

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[6] Patty, *Am. J. Pub. Health*, **30**, 1191 (1940).

the paper becomes dry, it should be moistened with alcohol before use. It is said to give a specific reaction for phosgene.[7, 8]

b) *Test Solutions*

1. A very sensitive drop reaction is described by Anger and Wang.[9] Add a drop of phenylhydrazine cinnamate to a drop of the solution of the suspected substance in chloroform or carbon tetrachloride. After 5 minutes, add a drop of 1 per cent copper sulfate solution. The red-violet color of diphenylcarbazide is formed in the presence of phosgene. As little as 0.0005 mg. of phosgene can be detected by this method. A variation of this test is to use filter paper impregnated with copper sulfate, dried and dusted with phenylhydrazine cinnamate. In the presence of a drop of water, phosgene produces the violet color if the concentration is 1 in 50,000.[9, 10]

2. The following modification of the diphenylurea test can also be used. Phosgene forms diphenylurea when passed into an aqueous solution of aniline. Pass the suspected air through about 3 ml. of a saturated aqueous solution of aniline or *p*-phenetidine. A white turbidity and then a crystalline precipitate forms in the presence of phosgene.[11, 12]

Quantitative methods for the determination of phosgene are given by Jacobs.

5. DIPHOSGENE, $ClCOOCCl_3$

1. Diphosgene will react with the test papers described for phosgene.

2. Diphosgene reacts only feebly with cold water but with hot water, it decomposes forming hydrochloric acid. It is decomposed on heating or on contact with porous materials into two molecules of phosgene. By passing the suspected gas through a tube heated at 300–350° C., the substance is completely decomposed into phosgene and may be detected and estimated by the methods detailed for that compound.

3. When an atmosphere containing diphosgene is passed into a solution containing an excess of sodium phenate, a white precipitate of diphenylcarbonate, insoluble in cold water and with a melting point of 110–111° C. is formed.

4. If some of the ether extract is available, drop a little on pieces of broken unglazed porcelain and heat in a small quartz or Pyrex tube. Since primary phosgene is no longer present, the phosgene derived from the

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[7] Studinger, *Chemistry & Industry*, **56**, 225 (1937).

[8] Cox, *Analyst*, **64**, 807 (1939).

[9] Anger and Wang, *Mikrochim. Acta*, **8**, 24 (1938).

[10] Cox, *Analyst*, **64**, 807 (1939).

[11] Kling and Schmutz, *Compt. rend.*, **168**, 773 (1919).

[12] Hennig, *Gasschutz u. Luftschutz*, **7**, 18 (1937); *Chem. Abstracts*, **31**, 2311 (1937).

decomposed substance may be detected by means of test papers or as diphenylurea.

5. Diphosgene also reacts directly with aniline water upon shaking.

6. ETHYLBROMOACETATE, $CH_2BrCOOC_2H_5$

1. Ethylbromoacetate is slowly hydrolyzed by water with the formation of bromoacetic acid.

2. It is quickly absorbed by alcoholic potassium hydroxide solution with the formation of potassium bromide and glycollic acid. Glycollic acid may be identified by adding to the alkaline solution a small particle of guiacol and then a few drops of sulfuric acid. On warming, a violet color is produced. For quantitative estimation the amount of bromide may be ascertained.

The methyl ester, boiling at 144° C., is entirely similar in lachrymatory properties to the ethyl ester but is twice as potent. It may be estimated and detected in the same way.

7. ETHYLIODOACETATE, $CH_2ICOOC_2H_5$

1. It may be possible to detect this agent with starch-iodide paper, for the war gas often contains free iodine as an impurity.

2. Ethyliodoacetate can be detected in a manner entirely analogous to ethylbromoacetate. It is quickly absorbed by alcoholic potassium hydroxide solution with the formation of potassium iodide and glycollic acid. The glycollic acid can be identified by its reaction with guiacol and sulfuric acid. The presence of iodide, which is demonstrated by the addition of silver nitrate solution to yield a precipitate of silver iodide, is a good indication of the presence of ethyliodoacetate. Quantitative estimation can be made by determining the concentration of iodide.

8. METHYLCHLOROFORMATE, $ClCOOCH_3$

1. Methylchloroformate is decomposed by alkali with the production of methyl alcohol and hydrochloric acid, whereas the chloromethylchloroformates all produce chlorine as well as hydrochloric acid on alkaline hydrolysis and will therefore liberate iodine from potassium iodide.

2. By passing the gas through an alcoholic solution of aniline, hydrochloric acid is formed:

$$ClCOOCH_3 + C_6H_5NH_2 \rightarrow C_6H_5NH.COOCH_3 + HCl$$

By titration of the liberated hydrochloric acid the amount of methylchloroformate may be estimated.

9. CHLOROMETHYLCHLOROFORMATE, $ClCOOCH_2Cl$

According to Degand,[13] chloromethylchloroformate, Palite, gives a positive reaction with Harrison's test paper, that is with *p*-dimethylaminobenzaldehyde and diphenylamine test paper.

This chemical agent is hydrolyzed in aqueous solution at ordinary temperatures and more rapidly at elevated temperatures to formaldehyde, hydrochloric acid and carbon dioxide.

$$ClCOOCH_2Cl + H_2O \rightarrow HCHO + 2HCl + CO_2$$

The presence of formaldehyde may be detected by the formation of a red zone on adding a drop of 1 per cent phenol solution and underlaying with concentrated sulfuric acid. This reaction is not given by dichloromethylchloroformate or diphosgene.

Formaldehyde is also produced on the addition of sodium hydroxide solution and other alkalies.

10. BROMOACETONE, $CH_2BrCOCH_3$

1. Bromoacetone is only slightly soluble in water and is not decomposed by it. The vapor is quickly absorbed in warm 0.5 N alcoholic potassium hydroxide solution, forming potassium bromide and the hydroxyketone. The ketone formed may be identified by the addition of a few drops of sodium nitroprusside solution, which yields a red color with the acetone derivative. The color of the acetone derivative is intensified by the addition of acetic acid.

2. Another method is to pass the gas into sodium hydroxide solution, then add a few drops of an alcoholic solution of *o*-nitrobenzaldehyde, which combines with the acetone derivative to form indigo. This test is not as sensitive as the nitroprusside reaction.

3. If sufficient of the gas can be trapped in alcohol in the sampling device, it may be combined to form the nitrohydrazone with 2,4-dinitrophenylhydrazine. To 1 ml. of a 1 per cent alcoholic solution of dinitrophenylhydrazine, 1 drop of hydrochloric acid and a few drops of the alcoholic test solution are added. The mixture is kept at room temperature until crystals of the nitrophenylhydrazone separate. A few more drops of hydrochloric acid may help the crystallization. The melting point of the acetone compound is 148° C.[14]

4. Bromoacetone can be quantitatively estimated by trapping in alcohol, hydrolyzing with alcoholic potassium hydroxide in the presence of hydrogen peroxide and subsequent determination of the bromide ion formed.[15]

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[13] Degand, *J. pharm. Belg.*, **21**, 895 (1939).

[14] Cox, *Analyst*, **64**, 807 (1939).

[15] Flury and Zernik, *Schaedliche Gase*. Springer, Berlin, 1931.

5. Reduction of ammoniacal silver nitrate solution.—Absorb the gas on silica gel. Drop a granule into a test tube containing 5 per cent silver nitrate solution to which one quarter of its volume of ammonium hydroxide solution has been added. This reagent should be clear. If bromoacetone is present, silver is precipitated and both the granule and solution darken. This reaction is also given by chloroacetophenone, bromobenzyl cyanide and Lewisite.

11. BROMOMETHYLETHYL KETONE, $CH_2BrCOC_2H_5$

1. The chemical properties of bromomethylethyl ketone are similar to those of bromoacetone. The vapor is quickly absorbed in warm 0.5 *N* alcoholic potassium hydroxide solution with the formation of potassium bromide and the hydroxyketone, this gives an orange color with sodium nitroprusside solution, and a brown color with an alcoholic solution of *o*-nitrobenzaldehyde.

2. A nitrohydrazone can be formed with 2,4-dinitrophenylhydrazine in a manner analogous to bromoacetone. The melting point of the methylethyl ketone compound is 128° C.[14]

3. The vapor can be absorbed in an efficient bubbler containing alcohol. This sample test solution can be hydrolyzed with alcoholic potassium hydroxide solution in the presence of hydrogen peroxide and the bromide formed can be estimated by the usual methods.[15]

12. CHLOROACETOPHENONE, $C_6H_5COCH_2Cl$

1. Chloroacetophenone has adequate warning properties in very low concentrations and this irritant action may be used as a means of its detection.

2. It is not affected by water but can be hydrolyzed by warm alkaline solutions with the splitting out of chloride ion which can be detected in turn. Alcoholic extracts are to be preferred for the confirmatory tests.

3. It reacts with an aqueous alcoholic (1:1) solution of sodium sulfide to form diphenacyl sulfide melting point 77° C. and sodium chloride:[16]

$$2C_6H_5COCH_2Cl + Na_2S \rightarrow (C_6H_5COCH_2)_2S + 2NaCl$$

in which the chloride can subsequently be estimated. Appreciable quantities of the gas are necessary for this test.

4. When chloroacetophenone is passed into alcoholic ammonia, it forms indole, which can be oxidized to indigo by the addition of strong hydrogen peroxide solution or recognized by the red color produced on adding *p*-dimethylaminobenzaldehyde solution to the acidified test solution.

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[16] Hennig, *Gasschutz u. Luftschutz*, **7**, 18 (1937); *Chem. Abstracts*, **31**, 2311 (1937).

5. Chloroacetophenone reduces ammoniacal silver nitrate solution, see page 107.

6. It may be oxidized to benzoic acid by hot alkaline potassium permanganate solution as described below or the following procedure may be used.

Oxidation to benzoic acid.[17]—Place some granules of contaminated asbestos in a small tube sealed at one end. Add 0.1 ml. of an oxidizing solution prepared by dissolving 5 grams of potassium dichromate, $K_2Cr_2O_7$, plus 20 ml. of concentrated sulfuric acid in 100 ml. of water, and seal the tube. Heat at 200° C. in an air bath, surrounding the reaction vessel by a copper tube or gauze for protection. On cooling, crystals of benzoic acid may be observed. Transfer to another test tube, add 1 ml. of sulfuric acid and add a few crystals of potassium nitrate. Heat at 130° C. for 5 minutes. Cool, make alkaline with concentrated ammonia, add just enough water to dissolve the precipitated salts and a few ml. of sodium sulfide solution. In the presence of benzoic acid, a brown ring is formed.

The following solution of sodium sulfide may be kept in brown bottles without deterioration. Dissolve 5 grams of sodium sulfide in 25 ml. of water and add 25 ml. of glycerol. Dilute with 4 portions of water before use.

13. BENZYL BROMIDE, $C_6H_5CH_2Br$, AND XYLYL BROMIDE $CH_3C_6H_4CH_2Br$

1. Benzyl and xylyl bromides are only slowly decomposed by water but they are readily hydrolyzed by alkali.

2. When they are passed into an alcoholic solution of silver acetate, a precipitate of silver bromide is immediately produced.

3. When they are passed into a hot alkaline solution of potassium permanganate, benzoic or phthalic acid, respectively, is formed. The acids may be isolated by the use of ether and identified by the usual tests.

4. Benzoic acid test.—Aspirate the chemical agent into a hot alkaline potassium permanganate solution. Acidify with dilute sulfuric acid and extract with ether. Evaporate off the ether, dissolve the residue in water and add a drop of ferric chloride solution. A buff colored precipitate indicates benzoic acid formed by the oxidation of benzyl bromide.

An alternative procedure is to use an alcoholic extract of the sample. Filter the extract, remove the alcohol by warming on a steam bath, oxidize the residue with alkaline potassium permanganate solution and test as directed above. Chloroacetophenone also yields benzoic acid when oxidized in this manner.

5. Phthalic acid test.—Aspirate the chemical agent into a hot alkaline potassium permanganate solution. Acidify with dilute sulfuric acid and

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[17] Hoogeveen, *Chemistry & Industry*, **59**, 550 (1940).

extract with ether. Evaporate off the ether, and dissolve in a little alcohol. Add 1 ml. of 10 per cent sodium hydroxide to the alcoholic solution and evaporate to dryness on a steam bath. To the dry residue, add 5 ml. of concentrated sulfuric acid and warm for several minutes. Add 25 mg. of resorcinol and again heat for several minutes. Transfer the liquid to a test tube and heat to 160° C. for 5 minutes, using a paraffin bath. When cool, pour into 200 ml. of water and make alkaline. A characteristic greenish-yellow to brownish-yellow fluorescence will appear and is indicative of fluorescein derived from phthalic acid.

For small concentrations of phthalic acid, proceed as follows: To the alcohol solution placed in a porcelain dish or casserole, add 0.2 ml. of 10 per cent sodium hydroxide solution and evaporate to dryness on a steam bath. If necessary, the residue may be heated in a thermostatically controlled electric oven at 125° C., to obtain absolute dryness. To this residue add 5 ml. of concentrated sulfuric acid and warm on the steam bath for several minutes. Add not more than 25 to 40 mg. of resorcinol and again warm the mixture until solution is effected. Transfer the mixture to a test tube and heat in a paraffin bath at 160–170° C. for 10 minutes. Pour the cooled melt into 150 ml. of water and make alkaline with 10 per cent sodium hydroxide solution. If xylyl bromide was present in the sample, the characteristic greenish-yellow fluorescence of fluorescein is at once apparent when viewed against a black background. When viewed under the ultra violet lamp, the fluorescence is a light green.

14. DICHLOROMETHYL ETHER, $(CH_2Cl)_2O$

1. Although dichloromethyl ether is relatively insoluble in water, it is hydrolyzed by water even at ordinary temperatures with the formation of hydrochloric acid and formaldehyde:

$$(CH_2Cl)_2O + H_2O \rightarrow 2HCl + 2HCHO$$

The presence of formaldehyde may be detected as detailed on page 106 or by the tests described in the literature.

2. Dichloromethyl ether may be trapped in an alcoholic potassium hydroxide solution. This can be warmed to complete hydrolysis of the ether and the liberated chloride ion may be estimated by the Volhard method.

Group II a

1. HYDROGEN SULFIDE, H_2S

a) Lead Acetate Test

1. The atmosphere to be tested may be sampled by means of a hand exhausting pump with a barrel approximately 1.25 inches in bore and a

capacity of 126 ml. To the inlet end of the pump is screwed a spigot with an external screw to which a holder containing the test paper may be attached.

Test papers.—These may be made from Whatman No. 1 filter paper, cut into strips, 2 inches by 4 inches. The strips are impregnated with lead acetate solution, 10 grams of lead acetate dissolved in 100 ml. of water plus 5 ml. of glacial acetic acid. They are then suspended vertically in an atmosphere free from hydrogen sulfide, and left to dry at room temperature. One inch is cut off the top and bottom of each strip and discarded. These papers may be stored in a glass stoppered, air tight container, in which a drying agent, such as a silica gel capsule is present.

Method.—The lead acetate paper is clamped in a holder of special design, Fig. 1, which is screwed into the pump. The apparatus having been tested for leaks, a preliminary indication of the atmosphere to be tested is obtained by making two slow and steady strokes of the pump, and the paper is then removed from the holder and compared within 10 minutes with the standard color chart provided by the British Dept. of Scientific and Industrial Research. A positive test will be obtained if the concentration of the hydrogen sulfide is greater than 1 part in 60,000, (0.025 mg. per liter). If no stain has been produced, further tests are made with fresh lead acetate paper, this time increasing the number of strokes to 3 or 5. The concentration is read with the aid of the chart again. The stains obtained should be only on that side of the paper exposed to the gas entering the pump, and the back of the test paper should remain white or nearly so if the stain is very heavy.

2. It is clear that in the above method a known volume of air is drawn through the test paper. An alternative method of using lead acetate paper is the following.[18] The test paper is prepared by dipping filter paper into a solution containing 10 grams of lead acetate crystals in 100 ml. of 50 per cent glycerol. After removing the excess liquid with blotting paper, the strips of paper are placed in small glass tubes which are drawn out, evacuated and sealed. To test a sample of air or gas for hydrogen sulfide, connect the tube to the sample of air or gas by some suitable means, break off the end of the tube and as a result of the air or gas entering the tube, the paper will react with the hydrogen sulfide in this small volume. By comparing the depth of color produced with that obtained with air or gas containing known volumes of hydrogen sulfide, the approximate hydrogen sulfide concentration can be established. By increasing the size of the ampoule, and by having the ampoules of known volume, this test can easily be applied in the field for the quantitative estimation of hydrogen sulfide.

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[18] Woog, Sigwalt and Saint-Mars, *Bull. soc. chim.*, [5] **2**, 1214 (1935).

b) *Silver Cyanide Detector*[19]

The U. S. Bureau of Mines has developed a detector that provides a simple and fairly accurate means of detecting hydrogen sulfide. It is rapid in giving results, and accurate enough to indicate concentrations of hydrogen sulfide ranging from those that are harmless or but slightly harmful to those immediately dangerous to life. It will indicate hydrogen sulfide in the range of 0.0025 to 0.05 per cent.

The complete detector, Fig. 8, consists of a small inlet metal barrel corrugated on the end to permit a rubber tube to be attached, to which is attached a rubber aspirator bulb, a movable scale, and a tube containing the white granular reagent.

The reagents used in the hydrogen sulfide detector tubes consist of silver cyanide, AgCN on activated alumina, Al_2O_3.[20] The activated alumina serves as a carrier for the silver cyanide in a manner analogous to the pumice used in the hoolamite carbon monoxide tube, as explained on page 131. The chemical action which proceeds is given by the following reaction formula:

FIG. 8. Hydrogen Sulfide Detector. (*Courtesy Mine Safety Appliances Co.*)

$$2AgCN + H_2S \rightarrow Ag_2S + 2HCN$$

The reaction of the silver cyanide in the presence of hydrogen sulfide turns the white granules to a dark gray due to the formation of black silver sulfide. This begins at the end of the tube where the sample enters.

It should be noted that when the detector is used in the presence of hydrogen sulfide, hydrogen cyanide is liberated. This is an equally deadly gas. However, no anxiety should be felt regarding the use of the detector even in still air for the amount of hydrogen cyanide liberated is so small that the amount that can be formed by an entire tube is harmless even if the user inhaled the entire amount.

Assuming that the person using the detector is protected by suitable respiratory apparatus, the detector should be used as follows.

Break the tips of a detector tube, and insert the red end, which is the end that should always be placed in the detector so that it will be nearest the

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[19] Forbes and Grove, *U. S. Bur. Mines, Miners' Circ.* **33** (1938).

[20] Littlefield, Yant, and Berger, *U.S. Bur. Mines, Repts. Investigations*, **3276**, (1935).

aspirator bulb, through the tube guide at the top of the detector and place it in the opening directly above the aspirator bulb. Place the retaining head containing the inlet opening over the upper end of the detector tube. Slight pressure against the retaining head will insure a snug fit of the tube in the rubber seat. Loosen the thumb nut on the back of the detector and adjust the sliding scale until the zero is directly opposite the beginning of the chemical granules; then tighten the thumb nut. Squeeze the aspirator bulb 10 times, allowing it to expand completely each time. This will draw approximately 750 ml. of air through the chemical in the tube. Read the per cent of hydrogen sulfide on the scale midway between the longest and shortest ends of the gray discoloration of the detector tube. Temperature and storage have little effect on the tubes or the reaction. The commonly occurring gases do not interfere.

c) *p-Aminodimethylaniline Sulfate Method*[21, 22, 23]

Hydrogen sulfide may be estimated colorimetrically with *p*-aminodimethylaniline sulfate in the presence of zinc and iron.

Procedure.—Absorb the hydrogen sulfide in a gas absorption bottle containing 130 ml. of 1 per cent zinc acetate solution and 5 ml. of 10 per cent sodium hydroxide solution. Disconnect the absorption bottle after sampling a known volume of air and add 25 ml. of diamine reagent, prepared by dissolving 0.1 gram of *p*-aminodimethylaniline sulfate in 100 ml. of hydrochloric acid (1:1). Mix this reagent and the test solution with any remaining zinc hydroxide by a rapid whirling of the bottle. Add 5 ml. of 0.02 *M* ferric chloride solution, 0.02 *M* ferric chloride, $FeCl_36.H_2O$ in 4 per cent hydrochloric acid, and mix. A blue color develops which is proportional, after a 2 hour reaction, to the amount of hydrogen sulfide present. Transfer the blue solution to a 250 ml. volumetric flask, and dilute to the mark.

When the hydrogen sulfide amounts to 0.1 mg. or more, a blue color, which can be matched very readily with standards after 2 hours, is obtained. Quantities of hydrogen sulfide of less than 0.1 mg. have a tendency to form a greenish tinge which predominates over the blue in solutions after standing over night.

2. DIMETHYL SULFATE, $(CH_3)_2SO_4$

1. Dimethyl sulfate is slowly decomposed by cold water, rapidly by warm water and by alkalies with the formation of methyl alcohol and methyl sulfuric acid or with the production of sulfuric acid and methyl

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[21] Almy, *J. Am. Chem. Soc.*, **47**, 1381 (1925).

[22] Mecklenburg and Rosenkranzer, *Z. anorg. Chem.*, **86**, 143 (1914).

[23] Sheppard and Hudson, *Ind. Eng. Chem., Anal. Ed.*, **2**, 73 (1930).

ether. These may subsequently decompose to form formaldehyde and methyl alcohol.

Boil the absorbing solution containing the suspected gas for one hour under a reflux condenser and distill. The presence of methyl alcohol in the distillate and of free sulfuric acid in the residue, indicates dimethyl sulfate.

2. It may be estimated by slowly passing the air to be tested, or air through the sample being tested, through an alkali absorbing solution. Subsequently the amount of hydrolyzed sulfate present may be obtained by the barium sulfate method.

Group II b

1. DICHLOROETHYL SULFIDE, MUSTARD GAS, $(CH_2ClCH_2)_2S$

a) Test Papers

1. Sodium Iodoplatinate Paper.—Dilute 1 ml. of 5 per cent platinic chloride solution and 5.3 ml. of 5 per cent sodium iodide solution to 180 ml. with water. Allow to stand for 24 hours before using. Dip filter paper into this solution of sodium iodoplatinate and pass the air to be tested through the filter paper. First a purple-red and then a violet coloration develops.

The test depends essentially on the reduction of quadrivalent platinum to the bivalent state with a co-liberation of iodine.

2. Gold Chloride Paper.—Impregnate paper by immersion in a 10 per cent solution of gold chloride, $HAuCl_4 . 4H_2O$. Dry at 60° C. Used dry, a yellow or brown-red color is produced in the presence of mustard gas. This reaction is practically specific for mustard gas in the absence of reducing agents such as carbon monoxide or hydrogen sulfide. The latter may be eliminated by the use of a guard tube.

After exposure to the gas to be tested, place the paper in a drop of mercurous nitrate solution. The unchanged gold chloride is reduced to metallic gold but the mustard gas-gold chloride complex is not affected greatly and appears as a light spot against a black background.

3. Sudan Red Paper.—Prepare this test paper by dusting Sudan Red powder on the paper and lightly shaking off the excess. It may also be prepared by impregnation but in this instance is not as efficient an indicator. Sudan Red paper is used only for the detection of liquid mustard gas since it does not give a clear reaction with the vapor. The limitations noted for Sudan Red dusting powder on page 75, also apply to the test paper.

b) Test Solutions

1. Sodium Iodoplatinate Test.—Prepare the reagent sodium iodoplatinate as directed above. Aspirate the air containing the suspected gas through a tube open on both ends and containing glass wool wet with acetic acid free of oxidizing agents as directed on page 73; alternatively, pass the air through 1 ml. of 5 per cent acetic acid solution. Add 2 or 3 drops of iodoplatinate reagent, sufficient to produce a pink color and 2 drops of 1 per cent starch solution. The starch solution should be prepared fresh every few days by rubbing 0.1 gram of soluble starch to a paste with a little water and then pouring this paste into 10 ml. of boiling water. A blue color indicates mustard gas. Chlorine, nitrous fumes and other oxidizing agents also give positive reactions, while reducing agents including the arsenical vesicants tend to decolorize the reagent. Phosgene, diphosgene, chloropicrin, ethyliodoacetate and bromobenzyl cyanide, however, do not affect the reagent.

2. **Gold Chloride Test.**[24]—This test depends on the yellow addition product formed between gold chloride and mustard gas, page 113.

Place one drop of 0.1 per cent solution of gold chloride in the constricted bend of a U-tube, one arm of which is blown into a bulb, in such a way that air drawn through the tube bubbles through the liquid. For transportation purposes, the ends of the tube may be closed with short lengths of rubber tubing in which are inserted glass rods. Connect the arm containing the bulb with a 250 ml. hand suction pump and connect the other arm through a dust filter with a metal funnel 10 cm. in diameter. Hold the funnel over the area on the ground to be examined, or place the material to be examined into the funnel. Draw the contaminated air through the reagent and note the first appearance of a turbidity. This may be most easily seen against a dark background, or, at night time by means of a blue light.

3. **Grignard's Test.**—This test depends upon the formation of diiodoethyl sulfide by the action of sodium iodide, in the presence of copper sulfate as a catalyst.[25] The sample should be warmed. It is not as sensitive as the gold chloride test.

Reagent.—Dissolve 20 grams of sodium iodide, 40 drops of a 7.5 per cent solution of copper sulfate, and 2 ml. of a 35 per cent solution of gum arabic in 200 ml. of water.

Procedure.—Bubble the air thought to contain mustard gas through 1 ml. of the reagent, or add a drop of the suspected solution of the gas. A yellow colloidal precipitate of diiododiethyl sulfide is formed in the presence of mustard gas.

4. **Sodium Sulfide Test.**—When mustard gas is passed through 1 ml. of a 20 per cent aqueous solution of sodium sulfide, a precipitate of diethylene sulfide is produced.[26] This compound melts at 111° C.

5. **β-Naphthol Test.**[26]—When mustard gas is passed into 1 ml. of a freshly

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[24] Schroeter, *Angew. Chem.*, **46**, 164 (1936).

[25] Grignard, Rivat and Scatchard, *Ann. chim.*, **15**, 5 (1921).

[26] Cox, *Analyst*, **64**, 807 (1939).

prepared alcoholic solution of β-naphthol mixed with an equal volume of 0.1 *N* sodium hydroxide, a turbidity, due to dinaphthylthioether, is produced with as little as 0.06 mg. of the gas.

6. Selenious Acid Test.[27]—Dissolve 1 gram of selenium dioxide, SeO_2, in 100 ml. of sulfuric acid (1:1).

Pass the suspected air through 10 ml. of the reagent in a bubbler or first pass air through the suspected material and then through the reagent. An orange-red suspension of precipitated selenium, which may be estimated nephelometrically, indicates the presence of mustard gas. This test is not specific, since it is also given by the derivatives of arsine, carbon monoxide and hydrogen sulfide.

c) *Tests on Solvent Extract*

The following tests may be made on the extract obtained as detailed in the scheme for the detection of war gases, page 84. These tests are generally applicable to war gases containing sulfur and a halogen.

1. Sodium Iodoplatinate Paper.—Dip filter paper moistened with a reagent solution of sodium iodoplatinate, Na_2PtI_6, into mustard gas or an aqueous mixture of it. First a purple-red and then a violet coloration develops.

2. Cerium Nitrate Test Paper.—Moisten filter paper with a 10 per cent solution of cerium or thorium nitrate solution and dry. Add a drop of the extract to the test paper and smoulder away in a fume hood. In the presence of mustard gas, thick heavy fumes of sulfuryl chloride, SO_2Cl_2, and sulfur trioxide appear.

3. Bleaching Powder Test.—Allow 1 drop of the extract to fall from the point of a knife on to dry bleaching powder or Perchloron powder (pure calcium hypochlorite) in a fume hood. Violent evolution of white vapors occurs. With Perchloron ignition occurs indicating oxidation of the mustard gas to oxides of sulfur and to sulfones.

4. Gold Chloride Test.—Shake a drop of the war gas extract with 1 ml. of water, filter and add to the clear solution 5–10 drops of a 0.1 per cent solution of gold chloride, $HAuCl_4$, solution. In the presence of the poison gas a yellow colloidal turbidity of fine oily droplets of the metal salt-mustard gas compound is formed. The test can be carried out with a dry test paper containing gold chloride. Addition of a drop of mustard and moistening produces a yellow spot of the molecular compound on the faintly yellow paper, as noted on page 113.

d) *Quantitative Methods*

Sulfate Test.—Mustard gas is the most important gas containing sulfur. Of lesser importance are dimethyl sulfate, methyl and ethyl ester of

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[27] Yablick, Perrott and Furman, *J. Am. Chem. Soc.*, **42**, 266 (1920).

chlorosulfonic acid, perchloromethyl mercaptan and thiophosgene. Eichler[28] describes a test in which the sulfide of mustard gas is estimated as sulfate after the elimination of interferences.

Procedure.—Pass a considerable quantity of air through 5 ml. of water in an efficient bubbler. Filter the resulting solution. Precipitate any hydrogen sulfide formed by means of cupric chloride solution and any sulfate by means of barium chloride. Filter. Oxidize any mustard gas present with potassium permanganate and precipitate the resulting sulfate as barium sulfate. As little as 0.07 mg. of mustard gas per liter of air is said to be detectable by this means.

Extraction and Titrimetric Method.—Mustard gas may not be recovered completely or at all, at times, from a polluted material by the aeration method. Lockwood[29] suggests a simple extraction and titrimetric method which may be used when it is desired to obtain a quantitative measure of the amount of mustard gas present. In this method mustard gas is extracted from a contaminated material by means of petroleum ether. The mustard gas is then re-extracted from this solvent by 66 per cent acetic acid and is estimated by titration with sodium iodoplatinate solution.

Reagents.—Purified petroleum ether.—Shake petroleum ether (boiling range 60–90° C.) in a separatory funnel with approximately one-tenth its volume of concentrated sulfuric acid at intervals for at least 2 hours. Separate the petroleum ether, wash 3 times by shaking with water, dry over anhydrous calcium chloride, filter and distill. This is unnecessary if the commercial petroleum ether gives a very small blank.

Sodium iodoplatinate solution.—See page 113.

Mustard gas solution.—Weigh accurately from 15–20 mg. of dichloroethyl sulfide into a capsule. Transfer the capsule to a 500-ml. flask containing glacial acetic acid, and dilute to volume with this reagent.

Blank test on reagents.—Transfer by means of a pipette, 25 ml. of petroleum ether and 50 ml. of glacial acetic acid to a dry separatory funnel and mix. Add 25 ml. of water, mix and allow to separate. Draw off the aqueous layer, filter and titrate as described below. The titration should not exceed 0.2 ml.

Standardization of sodium iodoplatinate solution.—Transfer a known aliquot, from 10 to 35 ml., of mustard gas solution to 25 ml. of petroleum ether in a separatory funnel and add sufficient glacial acetic acid to make the total volume of acid, 75 ml. Add exactly 25 ml. of water, shake, allow to separate, draw off the aqueous layer, filter and titrate as directed below. Repeat two times. Subtract the blank titration and calculate the value of 1 ml. of sodium iodoplatinate reagent. One ml. of the reagent is generally equivalent to 0.36 mg. of commercial mustard gas.

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[28] Eichler, *Oesterr. Chem.-Ztg.*, **40**, 81 (1937); *Chem. Abstracts*, **31**, 2962 (1937).

[29] Lockwood, *Analyst*, **66**, 480 (1941).

Procedure.—Weigh 40 grams of the material to be tested and transfer to a 200-ml. tall-form, wide mouth, glass stoppered bottle. Add 100 ml. of petroleum ether and shake at intervals for 1 hour. Filter 25 ml. by pressure into a 25-ml. pipette as follows: Equip a cork to fit the 200-ml. bottle with a 25-ml. pipette and a side tube for air pressure. Fit a small cork having a small hole with two 9 cm. filter papers, folded like a thimble and tie on with string. Place the small cork on the lower end of the pipette and immerse in the petroleum ether while applying air pressure. Transfer the filtered contents of the pipette to a dry, 125-ml. separatory funnel. Add 50 ml. of glacial acetic acid and shake, add 25 ml. of water, shake and allow to separate. Filter the lower layer through a dry filter and titrate as follows.

Add the dark red sodium iodoplatinate solution from a 5-ml. micro burette in volumes of 0.1 to 0.4 ml. at 1 minute intervals. The reagent changes to yellow in the presence of mustard gas in acetic acid. Take the slightest tinge of pink which persists after one minute as the end point.

The titration should not exceed 4 ml.; beyond this volume, the yellow color masks the excess red.

Under the conditions described, exactly half of the mustard gas originally in the 25 ml. of petroleum ether is transferred to the 75 ml. of 66 per cent acetic acid solution. This proportion holds, even in the presence of considerable amounts of fat. However, in analyzing a fatty material the volume of petroleum ether is adjusted according to the soluble fat content, on the basis that 1 gram of fat gives a volume in solution of 1.05 ml. For example, if the soluble fat content of the material is 28 per cent, the volume of petroleum ether required equals:

$$100 - \frac{28}{100} \times 40 \times 1.05 = 88 \text{ ml.}$$

Highly colored fats may interfere with the titration.

The titration should be carried out within an hour of adding the water to the mixture of petroleum ether and acetic acid.

Benzene, ethyl alcohol, amyl alcohol or acetone cannot be used as the solvent in this method. Thiodiglycol is not soluble in petroleum ether, consequently, it does not interfere.

White or wholemeal flour gives high results with the method as outlined above. To overcome this difficulty, mix 40 grams of the flour with 50 ml. of cottonseed oil and filter in a small press after 45 minutes. Add 12.5 ml. of the extract to 12.5 ml. of petroleum ether and continue with the method.

2. METHYLCHLOROSULFONATE, CH_3OSO_2Cl, AND ETHYLCHLOROSULFONATE, $C_2H_5OSO_2Cl$

1. Methyl and ethylchlorosulfonate differ from dimethyl sulfate in that they are hydrolyzed by water with the formation of methyl and ethyl-

sulfuric acid and hydrochloric acid. The presence of both free sulfuric and hydrochloric acids in the products of hydrolysis characterizes these agents.

2. By passing the air containing these gases through a bubbler containing alcoholic potassium hydroxide, the compounds are hydrolyzed to the potassium salts of hydrochloric and sulfuric acid and the corresponding alcohol. The methyl ester can be detected by the presence of methyl alcohol in the distillate. The amount of sulfate and chloride can be determined by the usual methods.

3. PERCHLOROMETHYL MERCAPTAN, CCl_3SCl

This chemical agent is hydrolyzed by hot water to yield carbon dioxide, hydrogen sulfide, hydrochloric acid and chlorine. Sulfur is precipitated on boiling. It may be recognized by making tests for some of the decomposition products mentioned.

4. THIOPHOSGENE, $SCCl_2$

This chemical agent is hydrolyzed in aqueous solution, yielding hydrogen sulfide and hydrochloric acid. It, too, may be recognized by its decomposition products.

5. SULFURYL CHLORIDE, SO_2Cl_2, AND CHLOROSULFONIC ACID, $ClSO_2OH$

1. Sulfuryl chloride and chlorosulfonic acid are rapidly decomposed by hot water with the formation of sulfuric acid and hydrochloric acid. Chlorosulfonic acid is probably formed as an intermediate stage in the decomposition of sulfuryl chloride. This reaction is also obtained with alkalies, the salts of the corresponding acids being formed.

2. Sulfuryl chloride is decomposed when passed through a glass tube heated to red heat with the formation of sulfur dioxide and chlorine.

$$SO_2Cl_2 \rightarrow SO_2 + Cl_2$$

The presence of both sulfur dioxide and chlorine is characteristic of sulfuryl chloride.

6. THIONYL CHLORIDE, $SOCl_2$

Thionyl chloride is decomposed by water with the formation of hydrochloric and sulfurous acids. The latter distinguishes it from the hydrolysis of sulfuryl chloride, chlorosulfonic acid and its esters.

It may be estimated by slowly passing a measured volume of contaminated air through a silver nitrate solution acidified with nitric acid. The precipitated silver chloride may be redissolved in ammonia and then reprecipitated with nitric acid.

7. SULFUR MONOCHLORIDE, S_2Cl_2

Sulfur monochloride is hydrolyzed by water with the formation of hydrochloric acid, sulfur dioxide and sulfur.

$$2S_2Cl_2 + 2H_2O \rightarrow SO_2 + 4HCl + 3S$$

The sulfur may arise from an intermediate reaction in which sulfur monochloride decomposes to form hydrochloric acid, sulfur dioxide and hydrogen sulfide.

It may be detected and estimated in a manner analogous to that given for thionyl chloride by passage of the contaminated air through silver nitrate solution acidified with nitric acid.

Group III a

1. HYDROGEN CYANIDE, HCN

a) Test Papers

1. Benzidine and Copper Acetate Test.[30]—The benzidine and copper acetate test is one of the more widely used tests for the detection of hydrogen cyanide in atmospheres. It depends upon the production of a blue color with moist, freshly prepared benzidine and copper acetate test paper in the presence of hydrogen cyanide. This color is produced in periods varying from 3 to 30 seconds depending upon the concentration of hydrogen cyanide. The test may be made by aspirating the gas through the test paper.

Reagents.—(1) Copper acetate solution.—Dissolve 2.86 grams of cupric acetate, $Cu(C_2H_3O_2)_2 \cdot H_2O$, in water and dilute to 1 liter. (2) Benzidine acetate solution.—Dilute 475 ml. of saturated benzidine acetate solution with 525 ml. of water.

Procedure.[31]—Mix equal parts of the cupric acetate solution and the benzidine acetate solution just before using. Dip slips of filter paper into the mixed reagent and take into the compartment to be tested in closed tubes or vials. Open the tubes and note the time to the second. Upon exposure in an atmosphere of hydrocyanic acid, the test paper will show a color varying from a very faint to an intense blue, indicating from 20 to 80 mg. hydrocyanic acid per cubic meter.

British Modification.[32, 33]—The official British modification of the benzidine copper acetate test is the following. Reagents.—(1) Benzidine acetate solution.—Heat two to three grams of pure benzidine acetate in 100 ml. of water for 10 to 15 minutes at 80° C. with constant stirring.

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[30] Sieverts and Hermsdorf, *Z. angew. Chem.*, **34**, 3 (1921).

[31] Sherrard, *U. S. Pub. Health Service*, Reprint No. 1224 (1928).

[32] *Dept. Sci. Ind. Research Brit.*, Leaflet No. 2 (1938).

[33] *Analyst*, **63**, 658 (1938).

When cold, filter the mixture by suction. The filtrate will contain about 1 per cent of benzidine acetate.

(2) Copper acetate solution.—Dissolve three grams of cupric acetate, $Cu(C_2H_3O_2)_2 \cdot H_2O$, in 100 ml. of water.

Immediately before the test is made, mix 25 ml. of the benzidine acetate solution with 2 ml. of the copper acetate solution and stir well. The mixed reagent will not keep more than 15 minutes.

The test papers may be prepared from extra thick white filter paper cut into strips 2 inches wide. Immerse them in the mixed reagent for 1 minute, drain and allow to dry in a warm atmosphere. Cut off one inch at the top and bottom of the strip and discard. Cut the remainder of the strip into 3-inch lengths. The papers must be used immediately.

To test an atmosphere for the presence of cyanide, the following procedure may be used. Place a prepared test paper into a holder and attach to a hand exhausting pump which has a barrel of approximately 1.25 inch bore and a capacity of 125 ml. Make a preliminary test of the atmosphere by making eight slow and steady strokes with the pump. Remove the paper and compare with the stains on standard charts.[32] In this way an estimate may be made of any concentration between 1 part in 10,000 and 1 part in 20,000 of air by volume, the latter being the maximum that can be inhaled for 1 hour without serious disturbance. If the stain indicates a concentration greater than 1 part in 20,000 a fresh paper is placed in the holder, and further tests are made with 1, 2, 3 or 5 strokes of the pump; or if a concentration of less than 1 in 100,000 is indicated, a rough estimate of the concentration may be obtained by repeating the test with a greater number of strokes of the pump, until a stain equal to one of the standards is obtained. Comparison of the stains should be made in diffused daylight or with the use of a daylight lamp.

2. Methyl Orange-Mercuric Chloride Test.[34]—This test depends on the change in color produced in a methyl orange-mercuric chloride test paper by hydrocyanic acid. The color changes from orange to pink. These test papers may be prepared in advance at a convenient place and will keep under proper conditions of humidity for as long as 30 days.

Reagents.—(1) Mercuric chloride solution.—Dissolve 1.25 grams of mercuric chloride in 250 ml. of water.

(2) Methyl orange solution.—Dissolve 0.60 grams of methyl orange in 250 ml. of water.

Mix 10 ml. of mercuric chloride solution with 5 ml. of methyl orange solution and add 1 ml. of glycerol. Immerse strips of Whatman No. 40 filter paper into the mixed reagent, and hang up to dry in air which is free from any trace of acid. When dry cut the filter paper into strips ½ inch wide and preserve in glass tubes protected from the light.

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[34] Sherrard, *U. S. Pub. Health Service*, Reprint No. 1224 (1928).

Procedure.—Suspend the test paper by means of a clip or other holding device in the place to be tested. Withdraw at the end of 2 minutes. A definite pink color at the end of two minutes exposure indicates a dangerous concentration of hydrogen cyanide gas in the air unless the humidity is great enough to accelerate the reaction. The test can also be made by carrying a small vial into the place to be tested and noting the change in color at the end of a known period of time. It is best to have two vials, one containing a strip of unaffected test paper, and the other containing a strip of paper with the pink danger color.

3. Picric Acid-Sodium Carbonate Test.—The picrate papers may be prepared by dipping filter paper strips, 2 inches by $\frac{3}{4}$ inch, into a solution containing 1 gram of picric acid and 10 grams of sodium carbonate dissolved in 100 ml. of water, and then drying the papers in room air. The papers may be prepared as much as a week in advance. The test paper is used dry and in the presence of hydrogen cyanide changes color from yellow to tan to brown within a time period of 5 minutes depending upon the hydrocyanic acid concentration.

b) Test Solution

Reaction with Ammonium Sulfide and Ferric Chloride.—Aspirate air over the heated granules into 2 ml. of alcoholic potassium hydroxide solution. Heat the absorbing solution in a water bath at 80° C. for 15 minutes, cool, acidify with 1 ml. of 25 per cent sulfuric acid and close with a stopper having an inlet and outlet tube. Connect with another tube equipped with inlet and outlet tubes similar to the arrangement shown in the latter half of Fig. 5 of the air-flow apparatus. The inlet tube of the second bubbler should dip into 2 ml. of yellow ammonium sulfide solution prepared by saturating concentrated ammonia with hydrogen sulfide while blowing air through at the same time and then diluting the resulting solution with an equal volume of 25 per cent ammonium hydroxide solution.

Draw air through the system and transfer the hydrogen cyanide evolved to the yellow ammonium sulfide solution. Remove the bubbler after 15 minutes and transfer the ammonium sulfide solution to a porcelain dish. Evaporate to about 3 drops. Add 3 drops of *N* sulfuric acid and a few drops of 1 per cent ferric chloride solution. A red color indicates the presence of ferric thiocyanate, $Fe(CNS)_3$. The limiting concentration is 0.01 per cent. A blank should be run on the reagents.

Other methods for the detection and determination of hydrogen cyanide and cyanides are detailed by Jacobs.[35]

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[35] Jacobs, *The Analytical Chemistry of Industrial Poisons, Hazards and Solvents.* Interscience, New York, 1941.

Group III b

1. CYANOGEN CHLORIDE, $CNCl$, AND CYANOGEN BROMIDE, $CNBr$

1. Sodium sulfide test paper.—Aspirate the gas to be tested through a paper soaked in a saturated sodium sulfide solution and used moist.

$$CNBr + Na_2S \rightarrow NaCNS + NaBr$$

Add one drop of concentrated hydrochloric acid, followed by a few drops of 1 per cent ferric chloride solution. A red color due to ferric thiocyanate indicates the presence of a hydrogen halide.

Since both cyanogen chloride and bromide are very volatile, it is best to carry out this test on the original sample rather than by absorbing the gases on activated charcoal or silica granules before applying the test.

2. Cyanogen bromide reacts with hydrogen sulfide, hydrogen iodide and sulfur dioxide to yield hydrogen cyanide. This may be detected as explained. Cyanogen chloride undergoes a similar reaction with hydrogen iodide but its reaction with hydrogen sulfide is more complex, since thiocyanic acid is also formed.

3. Cyanogen bromide will give the Prussian blue reaction but cyanogen chloride must be converted to hydrogen cyanide before this test can be applied.

4. Add sodium hydroxide solution and boil. The cyanogen halides yield ammonia.

2. BROMOBENZYL CYANIDE, $C_6H_5CHNCBr$

1. Bromobenzyl cyanide is such a powerful lachrymator and has such adequate warning properties that these in themselves serve as means of detection.

2. Bromobenzyl cyanide gives a blood red color with Sudan red test paper, prepared by soaking filter paper in a dilute solution of the dye in petroleum ether. This color is, however, given by other agents, for instance chloropicrin and mustard gas. A similar reaction in a more sensitive form can be obtained by passing the gas through a plug of absorbent cotton tinted with Sudan red by wetting the wool with a petroleum ether solution of the dye and drying the absorbent cotton.

3. It is quickly hydrolyzed by alcoholic potassium hydroxide solution, even in the cold, with the formation of potassium bromide and dicyanostilbene. This on boiling, gives off ammonia, and, if the solution is then cooled and acidified, a yellow precipitate of diphenyl maleic anhydride, which melts at 156° C. is obtained.

4. Concentrated sulfuric acid gives a deep red color on warming with a tiny droplet of bromobenzyl cyanide.

5. Aspirate the air containing the chemical agent through 10 per cent

silver nitrate solution, and boil. In the presence of bromobenzyl cyanide, reduction of the silver nitrate occurs and benzaldehyde, which may be detected by its characteristic odor, is formed.

6. Bromobenzyl cyanide also reduces ammoniacal silver nitrate solution. (See page 107.)

7. It should be noted that bromobenzyl cyanide, being in reality an isonitrile, does not give a cyanide reaction on hydrolysis with alcoholic potassium hydroxide and therefore cannot give a cyanide reaction unless benzyl cyanide is present as an impurity.[36]

3. CHLOROPICRIN, CCl_3NO_2

1. Dimethylaniline Reaction.—Preparation of test papers.—Soak strips of filter paper in a 5–10 per cent solution of dimethylaniline in benzene. Expose the paper which is white in color to the atmosphere to be tested, or if the concentration of the contaminant is low wave gently in the suspected atmosphere. The paper changes from white to yellow or maroon in the presence of chloropicrin. Chlorine, bromine and nitrous gases also give a color with this reagent but of a different shade.

2. Carbylamine Reaction.—Chloropicrin gives the Beilstein flame test for chlorinated hydrocarbons and because it has a trihalogenated carbon atom, it will give the carbylamine reaction. Pass the suspected gas into 2 ml. of hot alcoholic potassium hydroxide solution containing a drop of aniline and heat. The characteristic foul odor of phenylisocyanide results.

3. Sodium Sulfide Test.—Add 1 drop of gas extract, obtained as described in the extraction method given on page 84, to 5 ml. of 20 per cent sodium sulfide solution. Close the tube. Shake. The typical pungent odor of chloropicrin immediately disappears.

4. Nitrite Test.—When chloropicrin is passed into a solution of sodium ethylate, it is decomposed with the formation of chloride and nitrite:[37]

$$CCl_3NO_2 + 4C_2H_5ONa \rightarrow C(OC_2H_5)_4 + 3NaCl + NaNO_2$$

The presence of chloride can be demonstrated with silver nitrate and the Griess-Ilosvay reagent, can be used to show the presence of nitrite.

Reagents.—(a) Sulfanilic acid solution.—Dissolve 1 gram of sulfanilic acid in hot water, cool, and dilute to 100 ml.

(b) α-Naphthylamine hydrochloride solution.—Boil 0.5 gram of the salt with 100 ml. of water, kept at constant volume for 10 minutes. Decolorize with activated charcoal, if necessary.

If desired, a saturated solution of sulfanilamide may be used in place of (a) and a 0.1 per cent aqueous solution of N-(1-naphthyl) ethylenediamine dihydrochloride can be used in place of (b).

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[36] Cox, *Analyst*, **64**, 807 (1939).

[37] Hennig, *Gasschutz u. Luftschutz*, **7**, 18 (1937); *Chem. Abstracts*, **31**, 2311 (1937).

Dissolve 1 drop of poison gas freed from nitrous gases in 5 ml. of absolute alcohol, or aspirate the air to be tested through absolute alcohol. Add a small piece of 8 per cent sodium amalgam. After a few minutes decant the solution from the mercury. Acidify with acetic acid adding the acid drop by drop and then add 1–2 ml. of the Griess sulfanilic acid-α-naphthylamine reagent. After 10 minutes heat on a water bath. If much nitrous acid is present the red coloration will form even in the cold.

Chloropicrin can also be decomposed in this manner by passage through a methyl alcohol solution of potassium iodide, with the formation of chloride and nitrite:

$$CCl_3NO_2 + 4KI \rightarrow CI_4 + 3KCl + KNO_2$$

Add a few drops of acetic acid to this solution, then the Griess reagent and continue as above.[38] The presence of nitrite is practically specific as an indication of the presence of chloropicrin for other chemical agents containing nitro groups are seldom ever used.[39]

5. Diphenylamine Reaction.—The presence of nitrite may also be shown by the diphenylamine reaction. Pass the air through a few drops of concentrated sulfuric acid. Add a few crystals of diphenylamine. A blue color develops if nitrites are present. To confirm, add a small crystal of ferrous sulfate. A brown color indicates oxides of nitrogen. Chlorine, stannic chloride and titanium chloride produce a blue color also but do not give the confirmatory test.

6. Nitroso Reaction.—If sufficient of the sample is obtainable, a drop of the suspected sample is boiled with a 5 per cent alcoholic potassium hydroxide solution, or the suspected air is passed through the hot solution and a few crystals of resorcinol are added. A red color due to the formation of a nitroso compound is obtained on the addition of sulfuric acid.[40] With thymol a yellow color is produced without the addition of acid.

7. Combustion Methods.—Chloropicrin can be detected by combustion methods. If an atmosphere containing the gas is passed through a quartz tube heated to 450° C., the chloropicrin contaminant will decompose with the formation of chlorine.[41] This can be detected by bubbling through a potassium iodide solution containing starch solution as indicator. The liberated iodine will color the starch blue.

4. PHENYLCARBYLAMINE CHLORIDE, $C_6H_5NCCl_2$

1. Phenylcarbylamine chloride is not hydrolyzed by water and does not produce acid. Passed into hydrogen sulfide water it produces hydro-

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[38] Studinger, *Chemistry and Industry*, **56**, 225 (1937).

[39] Cox, *Analyst*, **64**, 807 (1939).

[40] Thompson and Black, *Ind. Eng. Chem.*, **12**, 1067 (1920).

[41] Fieldner, Oberfell, Teague and Lawrence, *Ind. Eng. Chem.*, **11**, 519 (1919).

chloric acid and phenylcarbylamine, so it may be recognized by adding a few drops of hydrogen sulfide water to a benzene solution of the gas or to the benzene which was used to trap the gas as the contaminated air was passed through it.

2. It gives the reactions for chloride and phenylcarbylamine on absorption by alcoholic potassium hydroxide solution.

3. Phenylcarbylamine gives a Grignard reaction resembling that of mustard gas, but may be distinguished from mustard gas by the absence of acid on hydrolysis and the absence of sulfur.

4. The test with Sudan red and ferric chloride diluted with chalk given by mustard gas is also given by phenylcarbylamine chloride,[42] page 76.

5. Pass the gas or air to be tested into water and boil. A white precipitate of diphenyl urea is formed if phenylcarbylamine chloride is present.

5. MONOCHLOROFORMOXIME, $ClCH{:}NOH$, AND DICHLOROFORMOXIME, $Cl_2C{:}NOH$

Heat the extract obtained as detailed on page 84, with concentrated hydrochloric acid to hydrolyze. Part decomposes to carbon dioxide and hydroxylamine and part to formic acid and hydroxylamine. The hydroxylamine can be detected in neutral or alkaline solution by the following tests:

(1) Nessler's reagent gives a grey-black precipitate of mercury.

(2) Reduction test.—Add 8 per cent sodium amalgam and heat. Ammonia is evolved and turns azolitmin test paper blue.

(3) Diacetylmonoxime.—This compound reacts with hydroxylamine to produce dimethyldioxime. In alcoholic solution, treat with a little nickel solution. Make slightly alkaline with ammonia or use an ammonium acetate buffer. A red precipitate forms.

Group IV a

ARSINE, AsH_3

1. The official British method for the detection of arsine in air uses a mercuric chloride test paper. Although silver nitrate test paper is about 20 times as sensitive as mercuric chloride paper, it has the drawbacks that the stains vary in color from yellow to black depending on the drying temperature. They continue to darken rapidly so that matching is difficult and the papers do not keep well. However, mercuric bromide test papers will do as well as mercuric chloride test papers.

In the British [43] standard test, the test papers are prepared by immersing the strips of filter paper in 5 per cent mercuric chloride solution, drying them, cutting off, and discarding the ends.

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[42] Ligtenberg, *Chem. Weekblad*, **34**, 321 (1937).

[43] *Dept. Sci. Ind. Research Brit.*, Leaflet No. 9 (1940); *Analyst*, **65**, 354 (1940).

The atmosphere under examination is drawn by means of a hand pump, described on page 67, through the test paper, and the resulting stain, if any is produced, is compared within 5 minutes with the standard stains issued with the leaflet. The concentration of arsine is then found by reference to the color chart, which shows the intensities of stains corresponding with 10 to 50 strokes of the pump. In this way concentrations of arsine down to 4 parts per million, that is 0.013 mg. per liter can be detected. The atmosphere to be tested is passed through lead acetate paper to absorb any traces of hydrogen sulfide before coming in contact with the mercuric chloride paper.

2. Arsine may be estimated quantitatively by absorption in potassium iodide solution acidified with sulfuric acid with subsequent titration of the liberated iodine. It may be determined by absorption in silver nitrate solution with subsequent titration of the resulting arsenious acid. It may be trapped in nitric acid, bromine or other oxidizing medium and then estimated by one of the methods detailed in Chapter V.

Group IV b

1. LEWISITE, CHLOROVINYLDICHLOROARSINE, $ClCH:CHAsCl_2$

1. Ilosvay Test.[44, 45] Reagent.—Place 1 gram of cupric nitrate, $Cu(NO_3)_2.5H_2O$, or the chloride or sulfate salt in a 50 ml. volumetric flask and dissolve in water. Add 4 ml. of concentrated ammonium hydroxide solution and 3 grams of hydroxylamine hydrochloride, $NH_2OH.HCl$. Shake until the mixture is colorless and make to volume. The reagent will last longer if made with the nitrate salt. If the reagent is covered with mineral oil, or if copper wire is added, it will retain its reactivity for a longer period. Paper impregnated with this reagent and used moist gives a red color with acetylene, due to the formation of cuprous acetylide.

When Lewisite is passed into 1 ml. of a 15 per cent sodium hydroxide solution, acetylene, sodium chloride and sodium arsenite are formed. Acetylene can be recognized by suspending a piece of cuprous chloride test paper above the alkali solution. The arsenic present can be shown by a direct test with the Gutzeit method.

2. As with other primary chloroarsines, a white precipitate of alkyl arsine sulfide is quickly produced on passing the suspected air or gas through a few ml. of water and then adding 3 drops of hydrogen sulfide water. Excess of hydrogen sulfide must be avoided, then the test is sensitive to 0.02–0.05 mg.[46] The turbidity or precipitate is soluble in ether. The test is also given by ethyldichloroarsine and methyldichloroarsine.

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[44] Ilosvay, *Ber.*, **32**, 2698 (1899).

[45] Treadwell and Hall, *Analytical Chemistry* (Vol. 2) Wiley, New York, 1915.

[46] Nametkin and Nekrassov, *Z. anal. Chem.*, **77**, 285 (1929).

3. Lewisite is rapidly hydrolyzed by water, producing hydrochloric acid and chlorovinylarsenious oxide. This aqueous solution will therefore yield reactions for acid, chloride and arsenic.

4. Aspirate the air or gas to be tested through an aqueous solution of mercurous nitrate acidified with nitric acid. Lewisite yields a white precipitate.

5. Lewisite gives the reaction with ammoniacal silver nitrate solution described on page 107.

2. METHYLDICHLOROARSINE, CH_3AsCl_2 AND ETHYLDICHLOROARSINE, $C_2H_5AsCl_2$

1. Methyldichloroarsine and ethyldichloroarsine are both quickly decomposed by water with the formation of the alkyl arsenious oxide and hydrochloric acid. Hence they give a test for acid, chloride and arsenic.

2. They both give the sulfide reaction with hydrogen sulfide water described under Lewisite, page 126, however no acetylene is formed when these compounds are absorbed by sodium hydroxide solution. This serves to differentiate them from Lewisite.

3. When these gases are passed into 1 ml. of mercurous nitrate solution just acidified with nitric acid, an immediate grey precipitate is formed with methyldichloroarsine, and a white precipitate, changing slowly to grey, is produced by the ethyl compound.

3. PHENYLDICHLOROARSINE, $C_6H_5AsCl_2$

Absorb the vapors or dust of phenyldichloroarsine in soda lime tubes.[47] Dissolve the contents of the tubes in hydrochloric acid and estimate the quantity of phenyldichloroarsine from an aliquot portion of the solution by the Gutzeit method.

The tests described for methyldichloroarsine and ethyldichloroarsine may also be applied to phenyldichloroarsine for it forms hydrochloric acid and phenylarsenious oxide on hydrolysis.

4. DIPHENYLCHLOROARSINE, $(C_6H_5)_2AsCl$

1. Test for secondary chloroarsines.—To an alcoholic extract of the sample, add an equal volume of 95 per cent alcohol saturated with hydrogen sulfide. Cool the mixture in ice water. Diarsines are precipitated when secondary chloroarsines are present.

2. Hydrolysis of an alcoholic extract of the sample with alcoholic potassium hydroxide solution yields potassium chloride and insoluble diphenylarsenious oxide, m. p. 92° C.

3. Diphenylchloroarsine is readily hydrolyzed by water also with the

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[47] Dudley and Jones, *U. S. Pub. Health Repts.*, **53**, 338 (1938).

formation of diphenylarsenious oxide. The presence of arsenic can be established by wet ashing and applying the Gutzeit test as described on page 92. An alternative method is to pass the dust into an acid potassium permanganate solution, which is decolorized and the arsenic may be subsequently determined.

4. The following method may be used to determine the amount of diphenylchloroarsine quantitatively.[48, 49] The dust is trapped in an efficient bubbler containing benzene, or chloroform, or the air sample may be taken in a large 10–15 liter bottle and the bottle washed with 30 ml. portions of the solvents by flushing the solvent around in the bottle. The volume of the benzene or chloroform solution is brought down to 10–20 ml. by evaporation, 20 ml. of a saturated solution of sodium bicarbonate is added and the solution is titrated with 0.01 or 0.001 N iodine solution. The number of ml. of 0.001 N iodine solution multiplied by 0.132 is equivalent to the amount of diphenlychloroarsine present in the air in mg.

$$(C_6H_5)_2AsCl + I_2 + 2H_2O \rightarrow (C_6H_5)_2AsOOH + 2HI + HCl.$$

Group IV c

1. DIPHENYLCYANOARSINE, $(C_6H_5)_2AsCN$

1. Diphenylcyanoarsine is only slowly affected by water but is quickly hydrolyzed by alcoholic potassium hydroxide with the formation of phenylarsenious oxide, and potassium cyanide. Upon the addition of acid, and warming while a piece of benzidine-copper acetate test paper is suspended in the vapor a blue color will be formed. See the tests for cyanides, pages 119–121.

2. The Prussian blue test may also be performed by the addition of a crystal of ferrous sulfate, a drop of ferric chloride solution, then boiling and acidifying with hydrochloric acid. This test is more sensitive and is specific.

3. The dust may be trapped by potassium permanganate solution or other oxidizing medium and then the arsenic may be estimated by the usual methods.

4. If a drop of the extract is obtainable, it may be melted with a little potassium hydroxide. The melt is then dissolved and the reactions for cyanide may be performed.

2. DIPHENYLAMINECYANOARSINE, $NH:(C_6H_4)_2:AsCN$

Diphenylaminecyanoarsine, Phenarsazine cyanide, is a toxic smoke similar to phenarsazine chloride, diphenylaminechloroarsine. In its

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[48] Hennig, *Gasschutz u. Luftschutz*, **7**, 18 (1937).

[49] Sieverts, *Z. angew. Chem.*, **35**, 17 (1922).

chemical reactions it is closely allied to diphenylcyanoarsine. Thus it is readily hydrolyzed by alcoholic potassium hydroxide with the formation of phenylaminearsenious acid and potassium cyanide. The presence of potassium cyanide may be demonstrated by tests previously detailed.

3. DIPHENYLAMINECHLOROARSINE, $NH:(C_6H_4)_2:AsCl$

1. Diphenylaminechloroarsine is slowly hydrolyzed by water with the formation of diphenylaminearsenious oxide. It can be detected and determined by the Gutzeit test as previously detailed.

2. The dust of this compound when passed into sulfuric acid will give a red color in the cold, which turns to blue if a trace of nitrite or nitrate is added. Alternatively, evaporate an alcoholic extract of the sample to dryness by gentle warming. Add a drop of concentrated sulfuric acid. An intense red color is produced, which changes to blue-green in the presence of nitrates, indicating diphenylamine, which is usually found as an impurity in industrial Adamsite.

3. Adamsite may also be detected by heating on a water bath with an aqueous solution of hydriodic acid which yields diphenylamine:

$$NH:(C_6H_4)_2:AsCl + 2HI \rightarrow (C_6H_5)_2NH + AsClI_2$$

The diphenylamine produced may be distilled with steam and detected as above with nitrite in sulfuric acid.

4. Remove the alcohol from an alcoholic extract of the sample by gentle warming. Add 5 ml. of a mixture of equal parts of 10 per cent silver nitrate solution and glacial acetic acid. In the presence of Adamsite, an intense yellow color is produced on standing for 10 minutes in a water-bath. Diphenylamine gives a dirty green color changing to black.

5. Diphenylaminechloroarsine gives the test for secondary chloroarsines detailed on page 127.

Group V a

CARBON MONOXIDE, CO

a) Canaries and Japanese Waltzing Mice

Small birds, such as canaries, may be used to detect carbon monoxide. Generally they will exhibit signs of distress and fall from their perch before sufficient carbon monoxide is present to affect a man. It has been shown that a man may feel only a slight headache at the end of 20 minutes in an atmosphere containing 0.25 per cent carbon monoxide, while canaries will show signs of distress in 1 minute and fall from their perch within 3 minutes.[50]

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[50] *Fed. Bd. Vocational Education*, Bull. No. 39 *Coal-Mine Gases*, (1931).

The United States Bureau of Mines[51] has shown that Japanese waltzing mice are equally as susceptible to carbon monoxide as canaries. These animals make erratic movements due to a physiological condition. The effect of a small fraction of 1 per cent of carbon monoxide is to quiet their movements immediately.

b) *Palladious Chloride Detector*

Ampoules.—The detector consists of an absorbent cotton covered, easily crushed, glass ampoule, which is filled with a palladious chloride solution that changes color when exposed to carbon monoxide, and a color chart. The procedure is to crush the ampoule, which in turn wets the absorbent cotton covering with palladium chloride solution. Expose it to the air to be tested. If carbon monoxide is present it will react with the palladious chloride and change the color of the ampoule from the brownish yellow stain of the solution to varying degrees of yellowish black to black, depending on the concentration of carbon monoxide.

The chemical reaction involved is a reduction of the palladious chloride by carbon monoxide to form a finely divided black precipitate of metallic palladium, while the carbon monoxide is oxidized to carbon dioxide. The finely divided precipitate of metallic palladium, which in appearance is much like carbon black, is deposited in the cotton fiber. The detector gives semiquantitative indications of carbon monoxide in a range of concentrations of 2 to 10 parts per 10,000 parts of air by volume when the temperature of the air is above 10° C. or 50° F. The sensitivity of the detector decreases with low air temperatures and a longer period of exposure than the prescribed 10 minutes is required to give a satisfactory indication of the amount of carbon monoxide present; 20 to 30 minutes are required for temperatures between 50° and 32° F.

It has been shown[52] that gasoline vapor, ethylene, hydrogen, and hydrogen sulfide produced a change in the color of the ampoules similar to that caused by carbon monoxide.[53, 54] Concentrations of these gases which produced the change, however, were also dangerous because of a hazard of either poisoning or explosion.

Test Papers.[55]—Another variation of this method is a device which consists essentially of a sheet of dry paper impregnated with a 2 per cent solution of palladious chloride and a sheet of plain paper held together between 2 plates of glass. The device is suspended in the suspected

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[51] Yant, Patty, Schrenk and Berger, *U. S. Bur. Mines, Repts. Investigations*, **3040**, (1930).

[52] Berger and Yant, *U. S. Bur. Mines, Repts. Investigations*, **3030** (1930).

[53] Sayers and Davenport, *U. S. Pub. Health Service*, Bull. No. 195 (1937).

[54] U. S. Patent 1644014.

[55] Chaignon, *15me Congr. chim. ind.*, **1936**, 261; *Chem. Abstracts*, **30**, 5464 (1936).

atmosphere for a definite time and in the presence of carbon monoxide the sensitized paper uniformly turns gray. Hydrogen sulfide produces a blackish brown coloration but only along the edges of the paper. The test can be made roughly quantitative by making the unsensitized paper into a series of panels of colors corresponding to increasing carbon monoxide contents and cutting a circle out of each panel through which the sensitized paper can be observed, so that the color produced on the sensitized paper can be compared directly with those of the various panels.

c) *Hoolamite Detector*

Hoolamite, $I_2O_5 + H_2SO_4 + SO_3$, activated iodine pentoxide, named after Hoover and Lamb[56] who patented the formula, is a mixture of iodine pentoxide and fuming sulfuric acid on granular pumice stone. When carbon monoxide comes in contact with this reagent, iodine is liberated, changing the originally white granules to bluish green of increasing depths. then violet brown, and finally black, depending upon the concentration of carbon monoxide. The chemical reaction that liberates the iodine is:

$$I_2O_5 + 5CO \rightarrow 5CO_2 + I_2$$

Hoolamite averages approximately 12.29 per cent of iodine pentoxide, 51.89 per cent of sulfuric acid (47 per cent sulfur trioxide, SO_3), and 35.82 per cent of pumice granules. As moisture causes deterioration of hoolamite, it is marketed in small glass ampoules tapered at both ends and hermetically sealed.

This detector has largely replaced the use of canaries and mice, as it requires less care and attention under most conditions and is more accurate.[57]

The complete indicator comprises a metal barrel filled with activated charcoal, through which air is drawn by means of a rubber aspirator. The activated carbon absorbs other gases. The inlet end of the barrel has a corrugated tip, to which an extension sampling line may be attached. The air is then discharged by the aspirator through a small glass tube containing hoolamite. A comparison color tube having five permanent colors in pumice stone, graduated from 0.10 to 1.0 per cent of carbon monoxide, is placed alongside the hoolamite tube. The scale and tube are kept in position by holders firmly attached to the metal barrel. For a description of the operation of this detector and other models see Forbes and Grove.[57]

Other tests for carbon monoxide are described by Jacobs.[58]

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[56] Lamb and Hoover, U. S. Patent, 1321062 (1919).

[57] Forbes and Grove, *U. S. Bur. Mines, Miners' Circ.*, **33** (1938).

[58] Jacobs, *The Analytical Chemistry of Industrial Poisons, Hazards and Solvents,* Interscience, New York, 1941.

Group V b

1. WHITE PHOSPHORUS

White or yellow phosphorus is used as an incendiary and as a screening smoke. At times, particles of free phosphorus may become imbedded in a material such as a food and then will not burn to phosphorus pentoxide. White phosphorus is poisonous if consumed and may cause serious burns if touched; hence, it must be detected if its presence is suspected.

Suspend 50 grams of the sample in 75 ml. of water in an Erlenmeyer flask and add 10 ml. of 10 per cent tartaric acid. Suspend above the surface of the liquid a test paper moistened with a drop of silver nitrate solution. Warm the mixture to 40–50° C. for 15 minutes on a steam bath.

The blackening of the silver nitrate paper may indicate the presence of white phosphorus. Since this blackening may be due to other substances, such as hydrogen sulfide, formaldehyde or other reducing compounds, a positive test must be confirmed by a distillation test.

Add 200 ml. of water to a portion of the sample and distill in a dark room. The presence of phosphorus is indicated by the formation of a luminous ring in the upper portion of the flask. Its presence is also indicated by its characteristic odor.

2. PHOSPHATES

a) *Microcolorimetric Method*

Phosphorus in the form of phosphate reacts with ammonium molybdate to form a complex phosphomolybdate. This complex is reduced to form a molybdenum blue by the use of solutions of hydroquinone and sodium sulfite.[59, 60]

Reagents.—Ammonium molybdate solution.—Dissolve 25 grams of ammonium molybdate in 300 ml. of water. Dilute 75 ml. of concentrated sulfuric acid to 200 ml. with water and add to the ammonium molybdate solution.

Hydroquinone solution.—Dissolve 0.5 gram of hydroquinone in 100 ml. of water and add 1 drop of sulfuric acid to retard oxidation.

Sodium sulfite solution.—Dissolve 200 grams of sodium sulfite, Na_2SO_3, in water, make up to 1 liter and filter. Keep this solution well stoppered or prepare a fresh equivalent each time it is to be used.

Standards.—Potassium dihydrogen phosphate solution.—Dissolve 0.4394 gram of pure, dry potassium dihydrogen phosphate, KH_2PO_4, in water and make up to 1 liter. Dilute 50 ml. of this solution to 200 ml. Each ml. of the latter solution is equivalent to 0.05 mg. of phosphorus.

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[59] Briggs, *J. Biol. Chem.*, **59**, 255 (1924).

[60] *Methods Assoc. Official Agr. Chem.* (4th ed.) 1935.

Procedure.—Convert the phosphorus and phosphorus compounds to phosphate. Transfer to a volumetric flask and make to volume. Transfer a 5 ml. aliquot to a 10 ml. volumetric flask. Add 1 ml. of the ammonium molybdate solution, rotate the flask to mix and allow to stand a few moments. Add 1 ml. of the hydroquinone solution, again rotate the flask; add 1 ml. of the sodium sulfite solution and mix. Make to volume with water. Stopper the flask and shake thoroughly. Allow to stand 30 minutes for development of the blue color and compare immediately thereafter in a colorimeter with 2 ml. of the standard potassium dihydrogen phosphate solution treated at the same time with the same reagents as the test solution and in the same way. With either the test solution or the standard set at 25.0 mm. readings within 10 mm. that is, with a range of 20 mm., are accurate. If concentrations of the test solution are outside this range, larger or smaller aliquots of the sample solution should be used.

VII. DECONTAMINATION

GENERAL REFERENCES

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In Chapter I contamination was defined as the liquid, dust or vapor remaining on a material or a person after exposure to a persistent agent or a non-persistent agent in appreciable quantity. Decontamination implies the treatment of the polluted object, area or person in such a way that danger from direct contact has been eliminated and consequently dangerous vapor can no longer be given off to the surrounding air. For practical purposes, materials are considered decontaminated when this objective has been obtained, even if the polluted material has merely been buried or sealed and not decomposed or otherwise destroyed.

I. Types of Contamination

Civilians will be exposed to three principal sources of gas from air attack:

1. Heavy localized pollution from chemical bombs.
2. Fine spray from aircraft.
3. Gross spray from aircraft.

As has been previously explained, liquid splashes which will be derived mainly from chemical bombs and gross spray from aircraft are the main sources of pollution. The effect of chemical agents on various materials has been discussed at some length in Chapter III.

II. General Methods of Decontamination

There are relatively few gases which are likely to cause serious contamination. These, we have learned previously, are the vesicants or blister gases, principally mustard gas, Lewisite, ethyldichloroarsine and the persistent lachrymators. However, one must not overlook the necessity of decontaminating materials, especially absorbent materials, which have been polluted with liquid of relatively volatile agents. On page 79 an example of the difficulty of releasing hydrogen cyanide by air-flow analysis was cited. Such contamination would be dangerous,—almost as dangerous as that of the vesicants.

There are few methods and procedures which may be used for decontamination. Broadly speaking, these may be placed in the following groups:

1) Weathering.
2) Washing.
    a) With water
    b) With organic solvents.
3) Destruction.
    a) By chemical decomposition.
    b) By incineration.
4) Sealing or Burying.
    a) With sand or earth.
    b) With sodium silicate.

General and even special methods of decontamination do not lend themselves to exact definition. One cannot lay down strict rules for every situation. The chemical agent used, the concentration of the contaminant, the position of the contaminated area, its nature and importance, the state of weather, the degree or urgency of need of the area, are all factors which must be taken into consideration if decontamination is to be achieved with a minimum of effort, a minimum of decontaminating material and a maximum of effect. The choice of the method to pursue depends upon a knowledge of the principles involved.

The practical principles governing the use of decontamination methods are:

1) The identification of the chemical warfare agent.
2) The degree and extent of contamination.
3) The importance of decontaminating a particular object or area.
4) The availability of the method of decontamination.

One must know what the chemical agent is in order to decompose it expeditiously by the use of chemicals. In an analogous way the knowledge of the amount or degree of contamination enables one to calculate the amount of material which will have to be used. If the place is relatively unimportant, like a park or garden, decontamination may be left to the weather. It is necessary to avoid dissipating the resources of trained men and material in decontaminating objects and areas which can be left untouched without detriment to the public safety. If an object or place is of importance, such as a factory producing essential military supplies, every effort must be made to decontaminate it as rapidly as possible, for it is essential not only to safeguard life and property but imperative to sustain the flow of military supplies as well. If a chemical or solvent is unavailable, it is clear that one cannot use these methods of decontamination.

It is absolutely essential that decontamination should be performed only by trained personnel, adequately equipped with decontamination tools and material and properly clothed with protective clothing and gas masks. The attempts of untrained people to decontaminate material, clothing or food, should be completely discouraged, for such attempts may lead not only to the injury of the persons involved but also to the loss of the material and food.

1. WEATHERING

Allowing an area to become free of gas by waiting for the sun, wind, and rain to evaporate, disperse and wash away a chemical warfare agent is termed weathering. These are processes which obviously depend upon favorable meteorological conditions and cannot be considered decontamination in the usual sense of the term. In weathering, the war gas is physically removed, diluted, dispersed and sometimes decomposed so that it is no longer harmful.

However, when aeration, ventilation and heating are used for the salvage of foods, as explained on page 157 or the decontamination of clothing, then the term decontamination is being used in its ordinary meaning.

Effect of Weather

Temperature.—Liquid persistent or non-persistent agents will evaporate more quickly in warm weather; hence the danger from the vapor of the chemical agent will be greater. However, the length of time the agent will actually be present will be less.

In very cold weather a liquid, such as mustard gas, may freeze; consequently there will be little danger from the vapor, although direct contact with polluted objects will still produce burns. When the temperature rises again, there will be increased danger because vapor will be given off again.

Areas bombed or shelled with chemical agents during the night when the temperature is low may give off but little vapor. As the temperature rises under the influence of the sun, harmful concentrations of vapor may be produced.

Besides the direct effect which temperature has on the physical state of the chemical agent, there is also the effect of temperature upon the ability of the agent to penetrate and combine with objects polluted by the war gas.

Wind.—A high wind rapidly blows away non-persistent gases or the vapors arising from an area contaminated by persistent gases. This aids in the dispersal of the gas but creates some danger downwind of persistent gas contamination. This danger is greater if only a light wind, less than 10 to 12 miles per hour, is blowing. The danger from liquid contamination is not eliminated.

In the absence of wind, the rate of mixing of the toxic vapor and air will be slow; therefore the war gas may drift about in dangerous concentrations for a time. Under such conditions, a gas may penetrate into buildings where the rate of mixing is even lower, thus presenting another source of danger.

Rain.—Light rain has little effect upon either persistent or non-persistent gases but a heavy rain tends to wash the vapors out of the air and helps to wash away and decompose any liquid contaminant upon the ground.

Rising Air Currents.—When the sun shines brightly, the surface of the ground becomes warm by the absorption of heat. The ground reradiates this heat, warming the air above it. The warmed air tends to rise, causing currents of rising air. This is one of the most effective means for the dispersal of a chemical agent, for it is diluted by tremendous volumes of air and so becomes harmless.

Clouds and Fogs.—Clouds, overcast skies, and fogs are actually favorable to the use of gas, for such conditions are not conducive to rising air currents that will dissipate the vapor of warm gases.

Weathering is used chiefly when it is not practicable to decontaminate an area thoroughly because of the unavailability of decontaminating chemicals, the extent of contamination or the unimportance of the area. In such circumstances the area should be clearly posted with warning notices indicating the agent involved and the date of detection. It is best to have yellow boards about 30 x 15 inches bearing the words in bold black letters: **DANGER GAS.** If it is at all possible, people should be prevented from entering the area by roping off the contaminated area and posting sentries or wardens.

It should be clear that weathering is a slow process, particularly as regards the vesicants, mustard gas and Lewisite. Indeed, a building and its immediate surroundings may have to be isolated for at least 21 days, if weathering is to be the sole means of decontamination; vaporization may continue for that length of time, varying according to the meteorological conditions, as pointed out previously.

2. WASHING

Washing as a method of decontamination is actually a method of physical removal of the chemical agent. It should always be adopted, where practicable, particularly washing with water, in order to save chemicals or where the use of chemicals is not feasible.

a) Water

In washing away chemical warfare agents with water, two actions are involved. First there is the physical removal of the agents by the mechanical action of the water and second there may be a chemical decomposition, due to the hydrolysis of the agent by the action of the water. This second action will be discussed more fully in a subsequent section.

In general, when war gases are to be washed away by the use of water, the object or area to be cleansed is hosed down with a stream of water One must be careful in doing this to make sure that the first hosing is done with a gentle stream of water. Otherwise, the force of the stream may actually splash the war gas all over and increase the area of contamination instead of decreasing it. After the initial gross contamination has been washed away, a stronger stream may be used to insure thorough removal.

Care must be exercised to make sure that the wash water actually flows away to where it is no longer harmful. It must not be allowed to collect where it can still become a source of danger, for then the very purpose of washing is vitiated. If the wash water must flow into pools or ditches, they must be considered as contaminated areas and be posted as such. Where the water has no safe place to be discharged, some alternative method of decontamination should be used.

Wherever the washing method is used, care must be taken to see that the chemical agent does not collect in cracks and joints. Such places must be treated chemically.

It must be remembered that hosing removes only the superficial contamination. Where the gas has had time to soak in, mere washing is ineffective as a means of decontamination. The sooner washing can be undertaken after a gas attack, the more thorough will be the removal by this means.

Hosing may be done with water from hydrants connected to city mains, with stirrup pumps, with pressure sprayers and with street flushers. Where water must be conserved for fire fighting purposes it may be best to fill street flushers with whatever water is available, such as river or sea water.

The addition of alkaline soaps and washing soda to the wash water is often valuable, particularly in the washing of buildings, walls, floors, fabrics, rubber and leather.

b) Solvents

Many objects cannot be washed satisfactorially with water and many such articles will not readily absorb chemical agents. Such articles, for instance, machinery, weapons, tools etc. can be washed by swabbing the surface with organic solvents, like kerosene, mineral oil, non-leaded gasoline, petroleum ether, alcohol and the like. These solvents dissolve the chemical agent and thus remove it physically; in general the agent is not destroyed, however; hence some means of disposal of the contaminated swabs must be employed. It is best to burn the rags or other material used for swabbing. The wiping should be repeated several times and only fresh rags should be used in order not to spread the contamination.

This method is particularly effective on metal surfaces and on objects of a greasy or oily nature.

3. DESTRUCTION

The two principal types of decontamination in which the chemical agent is destroyed are (1) decomposition by means of chemicals and (2) by incineration. In the former, the war gas is converted to a harmless or relatively harmless chemical and in the latter the war gas is evaporated or is burned to an innocuous gas.

a) Chemical Decomposition

Decontamination by chemical decomposition of the war gas is a principal method of decontamination. The chief chemical decontaminants are water and chlorinated lime. Of lesser importance but useful on occasion are commercial hypochlorite solution with sodium bicarbonate solution, sodium carbonate, sodium sulfide solution, sodium hydroxide in glycerol, strong alkaline soap and water and others. Table 24 lists the principal war gases and their decontaminating agents or, as they are commonly termed, their neutralizing agents.

Water.—Water is the cheapest and undoubtedly one of the best decontaminating agents. We have previously mentioned its use in the physical removal of pollution by hosing down of contaminated areas. On page 153 its use in decontaminating clothing is discussed.

Hydrolysis is a chemical reaction of the double decomposition type in which water is one of the reacting substances. Most of the war gases react with water. Table 23 shows the products of this reaction.

Cold water hydrolyzes mustard gas slowly but hot water reacts with it much more rapidly. That is the basis of the method for cleansing clothes given on page 153. The reaction between mustard gas and water produces thiodiglycol which is not toxic and hydrochloric acid which is harmful, but the latter is diluted to such an extent by the water, that it too has no harmful effect. The reaction is

$$(ClC_2H_4)_2S + 2H_2O \rightleftarrows (HOC_2H_4)_2S + 2HCl$$

TABLE 23

REACTIONS OF WAR GASES WITH WATER AND ALKALI

WAR GAS	BEHAVIOR TO WATER	REACTION WITH WATER	REACTION WITH ALKALI
Chlorine	Soluble	$HCl + HOCl$	$NaCl + NaOCl$
Phosgene	Rapidly hydrolyzed	$HCl + CO_2$	$NaCl + Na_2CO_3$
Diphosgene	Ditto	Ditto	Ditto
Chloromethylchloroformate	Ditto	$HCHO + HCl + CO_2$	$HCHO + NaCl + Na_2CO_3$
Chloropicrin	Stable, v. sl. sol.		With KOC_2H_5, KCl, $KNO_2 + C(OC_2H_5)_4$
Phenylcarbylamine chloride	Stable		$KCl + C_6H_5NC$
Dimethyl sulfate	Hydrolyzes slowly	$CH_3OH + CH_3OSO_2OH$ $H_2SO_4 + CH_3OCH_3$	$NaOSO_2OCH_3 + CH_3OH$
Methylchlorosulfonate	Hydrolyzes	$HCl + CH_3OSO_2OH$	$NaCl + Na_2SO_4 + CH_3OH$
Ethylchlorosulfonate	Hydrolyzes	$HCl + C_2H_5OSO_2OH$	$NaCl + Na_2SO_4 + C_2H_5OH$
Ethylbromoacetate	Hydrolyzes slowly	$BrCH_2COOH + C_2H_5OH$	With alc. KOH, $KBr + CH_2OHCOOK$
Ethyliodoacetate	Stable		With alc. KOH, $KI + CH_2OHCOOK$
Methylchloroformate	Hydrolyzed by hot water	$CH_3OH + CO_2 + HCl$	$KCl + CH_3OH + K_2CO_3$
Bromoacetone	Stable, sl. sol.		With alc. KOH, $KBr + CH_3COCH_2OH$
Bromomethylethyl ketone	Stable		With alc. KOH, $KBr + CH_2OHCOC_2H_5$
Chloroacetophenone	Stable		$KCl + C_6H_5COCH_2OH$
Benzyl bromide	Very slowly hydrolyzed		$KBr + C_6H_5CH_2OH$
Xylyl bromide	Ditto		$KBr + CH_3C_6H_4CH_2OH$
Bromobenzyl cyanide	Stable		Alc. KOH, $KBr + [C_6H_5C(CN)]_2$
Diphenylchloroarsine	Slowly hydrolyzes	$HCl + [(C_6H_5)_2As]_2O$	$KCl + [(C_6H_5)_2As]_2O$

Diphenylaminechloroarsine	Insol., hydrolyzes very slowly	$HCl + [(C_6H_5)_2NHAs]_2O$	$KCl + [(C_6H_5)_2NHAs]_2O$
Diphenylcyanoarsine	Hydrolyzes slowly	$HCN + [(C_6H_5)_2As]_2O$	$KCN + [(C_6H_5)_2As]_2O$
Dichloromethyl ether	Hydrolyzes	$HCl + HCHO$	$NaCl + HCHO$
Mustard gas	Hydrolyzes slowly	$HCl + (HOCH_2CH_2)_2S$	$KCl + (HOCH_2CH_2)_2S$
Lewisite	Hydrolyzes rapidly	$HCl + ClCH{=}CHAsO$	$C_2H_2 + KCl + K_3AsO_3$
Methyldichloroarsine	Hydrolyzes	$HCl + CH_3AsO$	$KCl + CH_3AsO$
Ethyldichloroarsine	Hydrolyzes	$HCl + C_2H_5AsO$	$KCl + C_2H_5AsO$
Phenyldichloroarsine	Hydrolyzes	$HCl + C_6H_5AsO$	$KCl + C_6H_5AsO$
Hydrogen cyanide	Miscible	Polymerizes $HCOONH_4$	KCN
Cyanogen chloride	Hydrolyzes slowly	$HCl + HCNO$	$NaCl + NaCNO$
Cyanogen bromide	Hydrolyzes	$HBr + HCNO$	$NaBr + NaCNO$
Titanium tetrachloride	Hydrolyzes	$HCl + Ti(OH)_4$	
FS	Hydrolyzes	$HCl + H_2SO_4$	
Phosphorus	Reacts after oxidation to P_2O_5	H_3PO_4	

TABLE 24
CHEMICAL DECONTAMINATING AGENTS

WAR GAS	DECONTAMINATING AGENT
Chlorine	Alkali, solid or in solution, sodium thiosulfate
Phosgene	Steam, ammonia, alkali, sodium phenate, hexamethylenetetramine and other amines
Diphosgene	Same as the above
Chloromethylchloroformate	Alkali
Chloropicrin	Aqueous-alcoholic sodium sulfite, alcoholic potassium hydroxide, sodium sulfide and polysulfide
Phenylcarbylamine chloride	Sodium sulfide
Dimethyl sulfate	Steam, alkalies
Methylchlorosulfonate	Alkali
Ethylchlorosulfonate	Alkali
Ethylbromoacetate	Alkali, sodium thiosulfate
Ethyliodoacetate	Alkali, sodium thiosulfate
Methylchloroformate	Alkali
Bromoacetone	Alkali, sodium thiosulfate, potassium sulfide in soap solution
Bromomethylethyl ketone	Alkali, sodium thiosulfate, potassium sulfide in soap solution
Chloroacetophenone	Strong hot sodium carbonate solution, alkali, sodium thiosulfate
CNS	Hot solution of sodium carbonate and sodium sulfite
CNB	5% alcoholic sodium hydroxide solution or solution 5 parts sodium hydroxide in 20 parts of water and 75 parts of Carbitol
Benzyl bromide	Alkali
Xylyl bromide	Alkali
Bromobenzyl cyanide	Alcoholic alkali
Diphenylchloroarsine	Alkali, gaseous chlorine
Diphenylaminechloroarsine	Oxidizing agents like gaseous chlorine, sodium hypochlorite solution, hydrogen peroxide, chloramine-T, iodine in sodium bicarbonate solution, etc.
Diphenylcyanoarsine	Same as above
Dichloromethyl ether	Alkali
Mustard gas	Chlorinated lime and oxidizing agents in general, 1–3% sodium sulfide solution, hot water, steam, chlorine dissolved in CCl_4
Lewisite	Alcoholic sodium hydroxide, hydrogen peroxide
Methyldichloroarsine	Alkali, oxidizing agents
Ethyldichloroarsine	Alkali, oxidizing agents
Phenyldichloroarsine	Alkali, oxidizing agents
Hydrogen cyanide	Alkali
Cyanogen chloride	Alkali
Cyanogen bromide	Alkali
Titanium tetrachloride	Alkali, solid or solution
FS	Same as above
HC	None needed
Phosphorus	Alkali or none needed for smoke, copper sulfate for solid particles

Lewisite, on the other hand, is rapidly decomposed even by cold water:

$$ClCH:CHAsCl_2 + H_2O \rightarrow ClCH:CHAsO + 2HCl$$

with the formation of chlorovinylarsenious oxide and hydrochloric acid. Chlorovinylarsenious oxide is a relatively insoluble substance. The solid is vesicant, so that contact with it may result in severe burns. Consequently, after an area polluted with Lewisite has been decontaminated by the use of water so that there is no danger from the vapor of Lewisite, there is still danger from contact with the solid decomposition product unless it has been washed away.

Phosgene is also hydrolyzed by water with the formation of hydrochloric acid and carbon dioxide:

$$COCl_2 + H_2O \rightarrow 2HCl + CO_2$$

Other chemical agents that are hydrolyzed by water are listed on page 85, and in Table 23.

Chlorinated Lime.—Next to water the most important decontaminating chemical agent is chlorinated lime. Chlorinated lime, commonly called chloride of lime or bleaching powder is a white or grayish-white powder of variable composition. Its formula is generally written as $Ca(OCl)Cl.2H_2O$ or $Ca(OCl)_2.CaCl_2 + H_2O$, both of which give some idea of its composition. This product usually contains about 35 per cent of available chlorine. Commercial products are now obtainable, known as high test bleaching powder with trade names such as H. T. H. or Perchloron, which are essentially pure calcium hypochlorite; this material contains about 70 per cent of available chlorine.

Chlorinated lime is not very stable, for it readily gives up its chlorine when exposed to air or moisture. For this reason bleaching powder should be kept in air-tight containers until just before use.

Chlorinated lime is an important decontaminating agent because it reacts with the most important persistent agent, mustard gas, rendering it innocuous by oxidizing and chlorinating it with the formation of a number of substances such as carbon dioxide, chloroform, chloral, hydrochloric acid, dichloroethyl sulfoxide, etc. Dry bleaching powder has a violent reaction with liquid mustard gas in which flame and heat are evolved. In the reaction some of the mustard gas is volatilized. Because of the violence of the reaction, chlorinated lime must be mixed with some other substance which will act as a diluent. The principal diluents used are water, sand, earth and petrolatum.

A 1:1 mixture of chlorinated lime and water is known as *slurry*. This is generally made by mixing 2 gallons of water weighing approximately 16 pounds with 3 shovelsful of bleaching powder also weighing 16 pounds.

It is necessary to mix these ingredients thoroughly and to strain them through a strainer in order to avoid lumps. To prepare this mixture, add 2 quarts of water to the 16 pounds of chlorinated lime and work into a smooth paste. Add the remaining water and stir thoroughly.

Chloride of lime is very corrosive to most metals and to cotton fabrics, hence it must not be used where this corrosive action will cause excessive damage to material and equipment.

Strained slurry can be sprayed from 3-gallon pressure type commercial insecticide sprayers with but slight modification. It can also be used with flusher type washers. However, since it is so corrosive, as was mentioned above, it must not be allowed to remain in the apparatus for more than 30 minutes. Immediately after use, the apparatus or flusher must be disassembled, thoroughly cleaned, rinsed with clear water and all working parts should be reoiled.

Sometimes it is advantageous to use a thinner mixture of chlorinated lime with water. A cream can be made from about 2 pounds of chlorinated lime to every gallon of water. On the other hand, where it is necessary to have a stiff paste of this material, much more chloride of lime should be used.

When mixed with sand or earth, about 3 parts of sand or earth should be used for every part of chlorinated lime.

Another mixture of chlorinated lime that is useful, particularly for surfaces of an oily or greasy nature or where corrosive action is to be minimized, is that with petrolatum. Equal parts of bleaching powder and petrolatum are mixed to form an ointment. The surface to be decontaminated is first swabbed with a solvent, as explained on page 139, and is then smeared with bleaching powder ointment. This should be left in contact for a short time and should then be wiped off, leaving a thin film of the ointment.

Bleaching powder may not contain its normal amount of available chlorine. It is a safe rule to use 1 part of bleaching material, whether commercial hypochlorite solution containing 5–15 per cent available chlorine, regular chlorinated lime or high test chlorinated lime, to 1 part of inert material for each 10 per cent of available chlorine. Thus with 1 pound of 70 per cent Perchloron or H. T. H., 7 pounds of earth may be used; with 1 pound of 30 per cent commercial chloride of lime, 3 pounds of earth may be used; with 1 pound of 10 per cent available chlorine, 1 pound of earth may be used.

As a general rule, 1 pound of 35 per cent available chlorinated lime is required for the decontamination of each square yard of polluted area. The weight of chlorinated lime slurry, 16 pounds of water to 16 pounds of bleaching powder, required for 1 square yard of different surfaces is given in Table 25.

Whenever chlorinated lime is used for decontamination, the odor of chlorine may persist and mask the odor of any remaining mustard gas or other chemical agent. It is important to remember that a decontaminated building, room, object, material etc., must be carefully inspected to make certain that decontamination is complete before use. It is also important to bear in mind that chloride of lime is white in color, therefore when it is used to decontaminate an outside area, it should be covered with earth to make it less visible.

Sodium Sulfide Solution.—Sodium sulfide reacts with a number of the war gases and renders them relatively harmless. Mustard gas and chloropicrin are the main war gases for which sodium sulfide solution is used as the decontaminating agent. It may also be used for the decontamination of phenylcarbylamine chloride. It is generally used as a 1 per cent aqueous solution. It reacts somewhat more slowly than chlorinated lime in decomposing mustard gas. Since little heat is evolved in this reaction, no mustard gas vapor is driven off. A hot solution is more efficient than a cold solution. It can be used as a spray or mixed with sand in the ratio of one part by weight of the solution to four parts of sand. About 6 gallons of sodium sulfide solution are required to decontaminate each square yard of polluted area.

TABLE 25

SLURRY REQUIRED FOR 1 SQ. YD. OF CONTAMINATED SURFACE

KIND OF SURFACE	WEIGHT OF SLURRY	VOLUME OF SLURRY
	lbs.	*pints*
Smooth concrete road	1.0	0.75
Loose-surfaced macadam or gravel	2.0	1.5
Short grass, 3–5 ins.	3.0	2.2
Long grass and low brush	4.0 or more	3.0 or more

Bromoacetone and bromomethylethyl ketone are said to be readily decomposed by spraying with a potassium sulfide solution, prepared by dissolving 240 grams of commercial potassium sulfide in 140 ml. of soap solution and diluting to 10 liters.

Green Solution.—Green solution is prepared by dissolving 1 pound of sodium bicarbonate in 1 gallon of commercial hypochlorite solution. This solution has a green color which gives it its common name. It is less efficient for the destruction of mustard gas than chlorinated lime slurry but is less corrosive, hence it can be used with less damage to metals. It should be applied freely with the aid of rags and sponges.

Alkaline Solutions.—Aqueous, alcoholic and glycerol solutions of sodium hydroxide or of common lye are used for the decomposition of a number of the common war gases. Thus, for instance, ethyliodoacetate, bromoacetone, chloroacetophenone and the halogenated lachrymators as a class are decomposed by the use of a 1:1 mixture of 50 per cent sodium hydroxide and glycerol. The glycerol reduces the caustic action of sodium hydroxide. This mixture is particularly useful for the decontamination of materials polluted with ethyliodoacetate. If painted surfaces are cleansed with this mixture, the paint will be removed but, since ethyliodoacetate is soluble in paint, the removal of the paint is an appropriate procedure.

Lewisite may be decomposed by a solution of 10 per cent sodium hydroxide in a 30 per cent solution of glycerol in water.

Alcoholic solutions of sodium hydroxide are useful in decomposing bromobenzyl cyanide and chloropicrin. Sodium hydroxide destroys phosgene. Solutions of potassium hydroxide in water, alcohol or glycerol act in a manner entirely analogous to equivalent sodium hydroxide solutions.

Hot aqueous solutions of sodium carbonate decompose chloroacetophenone. Strong alkaline soap solutions are useful at times in washing fabric, leather and rubber particularly if this can be done within 5 minutes after contamination.

Ammonia, hexamethylenetetramine, and sodium phenate are used for the decomposition of phosgene.

Other Chemical Decontamination Agents.—Sodium thiosulfate may be used for the destruction of chlorine, ethyliodoacetate, bromoacetone, chloroacetophenone and similar halogenated lachrymators.

Alcoholic sodium sulfite solution reacts rapidly with chloropicrin.

Hydrogen peroxide can be used for the decomposition of Lewisite.

Oxidizing agents in general can be used for the decomposition of the toxic smokes like diphenylaminechloroarsine, mustard gas, Lewisite and the dichloroarsines. Chlorine dissolved in carbon tetrachloride is useful.

b) *Incineration*

When the object is of little value or when the object is very badly polluted or contaminated and damaged beyond repair, or if the cost of decontamination is excessive, it is best to destroy the article by burning.

Several precautions must be observed when articles are incinerated: (1) The burning should be carried out in the open air, away from occupied buildings where no danger can be caused by the vapor which is produced by the incineration. (2) The detail engaged in conducting the incineration must wear protective clothing and must work on the upwind side of the fire. (3) The fire should be kept burning briskly, so that the chemical agents will be consumed and not merely evaporated by the heat.

An incinerator equipped with a tall chimney in which there is a good draft may also be used for burning contaminated articles. The rags used in swabbing contaminated articles should be burnt in such an incinerator.

Areas of land covered with dry grass and underbrush, may be decontaminated by being burned over. In such cases care must be taken to see that there are no persons downwind of the site for such distance as to be endangered by the gas cloud that is given off. To assist in burning over an area, it may be sprayed with kerosene, gasoline or other available inflammable liquid with subsequent addition of dead vegetation or straw to prolong the combustion period.

4. SEALING OR BURYING

Earth or Sand.—Earth, sand, ashes, or sawdust may be spread over a polluted area to give temporary protection. This method does not destroy the chemical agent. It merely sets up a barrier for the evaporation of the chemical agents and thus decreases the hazard. The thickness of the layer applied should be not less than 3 inches. Such a seal is more effective if wetted with water. The moisture will aid in the slow hydrolysis of those agents hydrolyzed by water. This process is to be employed on an area which does not need to be used but which is near enough to cause disturbance if untreated.

Sodium Silicate Solution.—Sodium silicate, that is water glass, is used as a seal on surfaces like concrete or unglazed porcelain or tile which may have absorbed a liquid chemical warfare agent. Since it will be extremely difficult to decontaminate such materials completely by washing, weathering or chemical decomposition, it is necessary to make certain that they will cause no damage. This is done by first thoroughly decontaminating the surface by washing and chemical decomposition. Then any remaining agent is permanently sealed in by the application of two or three coats of sodium silicate solution, allowing the water glass to dry in between the application of the additional coats.

III. Special Methods of Decontamination

It must be understood that the general methods of decontamination are not mutually self-exclusive. Indeed, it is advantageous to use them in conjunction with one another. While most of the procedures described apply to the decontamination of mustard gas, one must remember that there are other war gases also. Fortunately, the methods described will in the main work for a large majority of the war gases. The procedures may be made clearer by taking some examples as given by Williams.[1]

Assume that mustard gas liquid has been discharged on to the floorboards of a first floor room. Two situations present themselves immediately.

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[1] Williams, *J. Roy. Sanit. Inst.*, **61**, 167 (1941).

The first is that the mustard gas liquid has soaked into the floorboards, and the second is that if water is used to hose the mustard gas away, the water will pour through the floorboards and ruin the ceiling below. Therefore the first attempt to cleanse the floor should be made by the use of chlorinated lime-sand mixture (1:3) by spreading the mixture on the floor and scrubbing vigorously with deck scrubbers. This is followed by sweeping the floor clean and burying the sweepings in the garden or an open space. On examining the floorboards again, it may seem obvious that the gas is still present, hence the process must be repeated. If the penetration is considerable, the polluted floorboards must be removed and immediately burned in the open air.

Imagine the brickwork of an old house to become sodden with liquid gas with vapor issuing into the room of which the contaminated wall is a part. On the outside of the wall, chloride of lime slurry is sprayed or painted on the polluted surface and the mixture is brushed thoroughly into the joints. On the inside of the wall a much thicker mixture must be used, namely, one composed of 15–16 pounds of chlorinated lime to every gallon of water, which produces a thick mass similar to plaster. This mixture is troweled on to the suspected part, being held in position by newspaper. This is immediately followed by a second and third coat and is finally left for 24 hours. At the end of this time the inner wall is bared and inspected to ascertain whether the gas has been removed. If any doubt exists, the process should be repeated.

Mustard gas remains on the surface of hardwoods, or at least its penetration is delayed. To remove the liquid gas from hardwood, a solvent may be found to be sufficient.

Softer woods are generally painted with several coats of oil paint. When paint has covered a surface, one cannot tell at a glance whether mustard gas has penetrated the enamel, paint or wood, so a modified incineration process is used. In these cases, the medium for burning is a painter's blowtorch or some similar device, because thin layers may be burned off at a time and the depth of pollution can be ascertained without causing too much damage. Possibly only a panel or even a door may have to be completely destroyed by incineration in a fire in an open space.

Since liquid mustard gas can penetrate concrete, which is porous, as noted above, some treatment must be used. The loose liquid must be either mopped or swabbed into a container containing chlorinated lime slurry, mopping continually from pail to floor until the superficial mustard liquid is removed. Paste slurry over the site and leave the mixture in contact with the polluted section for six hours, after which mop or swab up the whole section. As the possibility exists that some vaporization may subsequently occur from the war gas which has penetrated, the concrete floor should be painted over with a solution of sodium silicate and water, 1:4. This should be done by applying the first coat, allowing it to dry, washing off the surplus, again allowing it to dry and recoating.

One method for a timbered roof is to locate the polluted area and using the stiff mixture mentioned above of 15–16 pounds of chlorinated lime to a gallon of water; trowel on a thick layer. This can be kept in position by wrapping canvas or strong paper around it. The bleach paste should be left in position for 24 hours and the process should be repeated until free of gas.

If a material is polluted by a persistent lachrymator, even traces will cause irritation. Therefore some method of decontamination must be used. Ethyliodoacetate and similar lachrymators can be decomposed by spraying a mixture of glycerol and a 50 per cent solution of sodium hydroxide over the contaminated walls, floors, etc. The mixture should be applied at least twice, with a 2 hour interval between each application.

The following special methods of decontamination apply mainly to mustard gas pollution.

1. ROAD SURFACES

Treatment for Fine Spray for all Surfaces.—Fine spray will tend to evaporate with a fair degree of rapidity, hence, decontamination must be started promptly to be effective. In busy streets and through traffic roads, hose down with water, if possible, within 30 minutes. In all other instances allow the contamination to be dispersed by weathering.

Treatment for Gross Spray and Outer Zone of Bomb Contamination, for all Surfaces.—Hose down the area with water as quickly as possible for 10 minutes. Repeat this treatment. Pavements and sidewalks that must be used immediately should be brushed with a thin slurry of chloride of lime.

Treatment for Heavy Contamination Around Bomb Craters. (1) *Stone Facings.*—Brush chloride of lime slurry thoroughly into joints. Allow to remain in contact for 15 minutes. Finally hose down with water.

(2) *Wood Paving.*—Hose down with water for 15 minutes. If the jointing material is soft, cover with sand or earth. If heavy liquid splashes are visible, treat them with bleaching powder-sand mixture or bleaching powder-earth mixture and allow the decontaminating agent to remain in contact for 1 or 2 hours.

(3) *Tarred Macadam or Asphalt.*—Hose down with water for 15 minutes. Use chloride of lime slurry for heavily contaminated areas. The machines used for resurfacing asphalt surfaces may also be used to decontaminate such roads by remelting the asphalt. The war gas is destroyed by incineration.

(4) *Natural Earth, Grass, etc.*—Cover the contaminated area with 2 or

3 inches of fresh earth and leave to the processes of weathering. If the pollution is very heavy and near buildings that are occupied, it is best to add a top layer of a mixture of earth and bleaching powder (3:1).

(5) *Stone Paving and Concrete.*—Hose down with water for 10 minutes. Brush chloride of lime slurry thoroughly into the surface for 5 minutes. Treat the gutters in a similar manner. Finally hose down with water again.

2. BUILDINGS

There will be little need to apply special treatment for contamination by the vapor or light spray of chemical agents for the reasons previously given. The treatment, designated below, is for liquid contamination.

Stone or Brickwork.—Hose down with water only, if this can be done before the liquid contaminant has had sufficient time to soak in. Spray with the aid of a pressure type insecticide sprayer or similar device, or brush the surface with chloride of lime slurry and allow the slurry to remain in contact with the surface for at least 24 hours. Repeat this treatment.

Concrete Floors and Unglazed Tiles.—Hose down with water. Apply chloride of lime slurry and brush out thoroughly over the surface. Allow the decontaminating agent to remain in contact for 6 hours. Hose with water. Paint the surface with a solution of sodium silicate, that is, water glass, and allow to dry. Paint once more with sodium silicate solution and again allow to dry.

Glazed Tiles.—These tiles are less absorbent than unglazed tiles, hence they do not need as drastic treatment. Hose with water and treat with chloride of lime slurry particularly at the joints where the slurry should be rubbed in thoroughly.

Papered Walls.—Strip off the paper. Paint or spray on chloride of lime slurry. Apply alternate layers of bleaching powder paste, 16 lbs. chlorinated lime to 1 gallon of water, and newspaper to hold the paste in place and leave in position for at least 48 hours. Finally wash off the wall and treat it with sodium silicate solution.

Walls or Ceilings Painted with Water Colors or Kalsomine.—Use the same procedure as for papered walls. However, a fresh coat of water color paint or kalsomine may be applied afterward.

Painted Walls, Wood or Plaster.—If immediate treatment can be applied, use the procedure outlined above and finally repaint. If the contamination has been prolonged so that the war gas has had the opportunity to soak into the paint, the pain must be completely removed.

Wooden Floors.—Absorb any visible liquid with the aid of sawdust or earth which should subsequently be burned or buried. Scrub the surface with chloride of lime slurry, and with sand. Allow these decontaminating agents to remain in contact for 24 hours, then brush off and wash with water. Repeat the procedure two or three times if necessary. Boards soaked with vesicants or those which cannot be decontaminated by the above treatment, must be removed and burned.

Unpainted Woodwork.—The general procedure should follow that outlined for wooden floors. However, hardwood articles and moldings should first be swabbed with kerosene and then treated with an ointment of bleaching powder and petrolatum. This ointment should be left in contact for a short period, and then should be wiped off, leaving a thin film on the surface.

3. HOUSEHOLD ARTICLES

Since personal contact with furniture cannot be avoided, hasty decontamination methods should not be used. Every effort should be made to insure complete decontamination.

Hardwood Furniture.—Swab thoroughly with mineral oil or kerosene. Apply bleaching powder-petrolatum ointment and allow to remain in contact for at least 48 hours.

Upholstery.—All upholstery should be stripped from the wooden framework. In most instances it will be easiest and best to burn the coverings and padding and replace it with new material. When it is necessary to apply decontamination procedures, those outlined in the section on clothing will be suitable in most instances. In brief, they are:

Woolen Fabrics.—Immerse in boiling water for 1 hour. See page 155 about shrinkage.

Cotton Fabrics.—Treat as directed on page 155.

Leather.—Expose for a prolonged period in a stream of hot air, or treat as directed on page 155. It will probably be safest to destroy by incineration.

Padding.—Aeration or burning are the best.

Bedding.—Bedding should be handled in a manner analogous to that outlined for upholstery. Mattresses may be handled as directed on page 154 in a steam disinfector.

Carpets, Rugs, etc.—If only slightly polluted, hang these articles in the open air and allow to weather for 7 days in mild weather and for 14 days in cold weather. If wetted with a vesicant, spray the article with a solution of sodium hydroxide before hanging out to air in order to prevent the fabric from being rotted by the chemical warfare agent. Heavily contaminated articles should be incinerated if arrangements cannot be made to immerse them in boiling water for two hours.

Linoleum.—If the floor covering is only slightly polluted and is in good condition, treat with chloride of lime slurry. If it is worn and the felt or burlap base is contaminated also, it is best to destroy the linoleum by burning.

Metal Fittings.—Swab well with kerosene or gasoline and rub dry with clean cloths. At times, bleaching powder-petrolatum ointment may also be used for a short time.

China, Glass and Earthenware.—Boil in water or in a strong bleaching powder solution.

4. VEHICLES

Buses, Streetcars, and Closed Commercial Trucks.—If these vehicles are contaminated by spray, hose the exterior thoroughly with water. Wash handrails and other metal parts which have to be touched with lead-free gasoline or kerosene.

If they are contaminated by gross liquid pollution, hose down with a steady stream of water. Brush over the fabric stops and all woodwork including back and front steps with a thin slurry of chloride of lime. Swab all metal parts with lead-free gasoline or kerosene. Finally allow to weather for at least 24 hours.

If the interiors of these vehicles have been contaminated, they must be decontaminated by appropriate procedures. Upholstery should be removed and destroyed.

Open Delivery Trucks and Cars.—The general treatment outlined for buses will normally be adequate for these vehicles. If the inside is contaminated, it should be scrubbed with a mixture of chloride of lime slurry and sand. This should be left on for 2 hours and should then be washed off. The floors of such vehicles will not be safe to sit on if heavily contaminated and should receive the treatment outlined for wooden floors of buildings.

Private Cars.—Hose down thoroughly. Wash parts likely to be touched with kerosene or gasoline. Remove contaminated upholstery and treat as described on page 151.

5. CLOTHING

The principal processes used for the decontamination of clothing are (1) weathering, (2) immersion in warm water, used principally for leather goods, (3) boiling in water with or without soda or washing soda depending upon the type of textile, (4) steam treatment, directly or in a high-pressure steam disinfector and (5) chlorine plus steam treatment. The principles governing the use of a particular method for a given type of clothes are similar to those previously discussed in this chapter.

a) General Methods of Decontamination

Weathering.—In this process the clothes are hung as usual on hangers or with clothes pins on clothes lines in an isolated place which has some kind of roof to protect the clothes from rain. Each garment or part of a garment must be hung separately so that the air can get at it and the clothes should not be hung too closely together. The period required for exposure will depend upon the weather conditions, the best conditions being, as previously explained, a high wind and high temperature. In warm weather, at least 2 days exposure is necessary. In cool, cloudy weather, this method cannot be relied upon.

After boiling clothing contaminated with Lewisite, the clothing must be aired for a considerable length of time, about 14 days in order to be deodorized.

This process is limited only to the removal of vapor contamination. However, articles contaminated with liquid can be aired to reduce the degree of contamination but must be treated by one of the subsequent methods.

Immersion in Warm Water.—In this process the war gas is either hydrolyzed to an innocuous compound or a relatively harmless one, or is dissolved and is washed away. The method is generally used for materials which would be harmed by subjection to the action of boiling water, such as leather goods. The temperature of the water is kept between 50–55° C. and the articles are immersed in the bath for about 6 hours.

Boiling in Water.—In this process also the chemical warfare agents are hydrolyzed but more rapidly than in the preceding method by the action of boiling water and they form innocuous compounds or are washed away. The method can be used for all types of materials that are not harmed by boiling water. In general, the clothes to be decontaminated are placed in tanks or washing machines, are complete immersed and are boiled for from ½ to 2 hours depending upon the type of clothes. About 1 and 2 gallons of water should be used for each pound of clothes. During the boiling, the clothes should be rotated slowly about 3 or 4 times. Cottons, linens, canvas, or other textiles that are likely to be affected by free hydrochloric acid may be boiled in water containing 2 ounces of washing soda per 10 gallons of water.

Woolen clothes may be treated by the boiling process, according to experiments carried out by the British. However, certain precautions must be observed. In the decontamination of woolen clothing, soap or washing soda or other alkaline detergents must not be used, and during the boiling process the clothing must not be subjected to any scrubbing or rubbing action. Thus washing machines with rotating mechanisms cannot be used unless the rotation is done carefully by hand. The rubbing, scrubbing, and alkali aid in the felting of wool, causing it to shrink. Mere boiling in which these actions are avoided will thus have little shrinking effect on wools.

It is to be remembered that clothes dyed with dyes that are not wash-fast will tend to run. Since boiling is a drastic process, some damage may result to clothes treated in this manner but since they would be worse than useless if left contaminated, chances must be taken. Care in handling will minimize damage due to the decontamination process.

Steam Decontamination.—This process consists essentially of driving off the contaminant by evaporation induced by the temperature of the steam. In more elaborate processes, the evaporation is aided by vacuum treatment before and after the steam treatment. Wet clothes cannot be handled by the vacuum process, since a vacuum would be difficult to maintain as long as the clothes were wet.

The simplest type of steam disinfector not equipped with a vacuum device is a large metal can provided with a false bottom which serves to hold the contaminated clothing about a foot from the true bottom. Six to eight inches of water are poured into the space below the false bottom and the clothing is placed in the can. The disinfector is placed over a fire, and the top is covered so that some steam may escape. The capacity of this device can be increased by hanging additional clothing in an inverted canvas bag suspended over the can, the open end of the bag being tied around the sides of the disinfector.

In general, the procedure used in the vacuum-steam type of disinfector is the following. Withdraw the basket of the disinfector and load it with clothing suspended on hangers. Heat the jacket of the device by admission of steam, replace the cage holding the clothing and close the disinfector. Evacuate the device to about 20 inches vacuum, shut off the evacuating mechanism and admit steam until a pressure of 10 pounds above atmospheric pressure is reached. Maintain this pressure for about 30 minutes and again evacuate the disinfector but this time to 15 inches vacuum. Admit air until atmospheric pressure is reached, open up the device and remove the clothing. The entire operation should take about 1 hour.

Chlorine and Steam.—In this method the mustard gas vapor or liquid contaminating clothing is first oxidized to an innocuous compound by chlorine gas and the decontamination is completed by the use of steam. When clothing treated with chlorine gas shows evidence of a white crystalline substance, it indicates that the clothing has been splashed with liquid mustard gas. This crystalline substance should be brushed off, if at all possible, before steaming. The chlorine treatment must be given before the steaming for best results.

Hang the clothing in inverted canvas bags. Run chlorine gas from a cylinder into the canvas bags by means of a rubber tube or pipe. Shake the bags at intervals to insure better contact between the clothing and the chlorine. Continue treating with chlorine for 10 to 15 minutes for vapor contamination and for 30 minutes for liquid pollution. Steam for 0.5

hour for vapor contamination and for 1 hour for liquid contamination as directed on page 154.

b) *Special Methods of Decontamination*

Woolens.—Boil the articles in plain water for ½ hour if the process is carried out in laundry machinery or for 1 hour if boiled in improvised tanks. Such articles of clothing, if dry, may also be treated by the steam-vacuum process. It must be remembered that no soap, washing soda, or other alkali is to be used and no rubbing or scrubbing of woolen goods. If the clothing is oily or greasy, the boiling must be continued for double the length of time noted above.

Cottons, Linens, etc.—Boil for 2 hour in water to which has been added 2 ounces of washing soda per 10 gallons of water.

Burlap Bags, Canvas, etc.—Boil for 1 hour in water to which washing soda has been added in the proportion noted above.

Leather Articles.—Immerse articles made of vegetable, semichrome or chrome-tanned leathers contaminated with mustard gas in plain water at 50° to 55° C. for 6 hours. Chrome-tanned leathers may be treated more quickly by boiling in water. Decontamination with chloride of lime is impractical because of its destructive effect on all types of leather.

Anti-Gas Clothing.—Immerse these articles for 2 hours in plain water kept just below boiling, that is at 95–99° C. Care must be exercised in the handling of these articles of clothing in order not to remove or crack the film to which the clothing owes its impermeability. The clothing must be folded or hung in such a manner that no damage can result from friction. Since some of these types of clothing have a lower specific gravity than water, care must be taken to see that they are completely immersed. This is most easily done with the aid of special fittings. Since friction must be avoided, washing machines cannot be used for the decontamination of anti-gas clothing.

Rubber Articles.—Rubber articles may be decontaminated by boiling from 1 to 3 hours in plain water depending upon the type of rubber goods.

IV. Decontamination of Water

As explained in Chapter III, it would be difficult to pollute the water supply of a large city to a sufficient extent to render the water harmful because of the enormous amounts of chemical agent needed for this purpose. Furthermore, many of the chemical agents are relatively insoluble in water. Others react and hydrolyze to form innocuous compounds. Still others react with some of the compounds in water to form harmless substances.

In any event, if the water purification system of the city is operating, the processes of coagulation, sedimentation, filtration, chlorination, etc., with the accompanying addition of alum and lime, ferrous sulfate and lime, activated carbon, ammonia, chlorinated lime, liquid chlorine or even ozone would tend to remove the war gases as a routine part of the potable water treatment process.

It is, of course, necessary for the proper local authority to keep a close watch on the potability of the water supply by performing chemical and bacteriological tests and to arrange to deliver pure water where any sectional pollution of water occurs.

Water supplies obtained from wells, cisterns, etc. and used as a private water supply must be analyzed by the proper authorities if any suspicion of gas pollution exists.

V. Decontamination and Salvage of Foods

The problems of decontaminating and salvaging foods may be difficult and some thought must be given to the method of cleansing in individual classes of food. Thus, for example, an expert butcher is obviously best qualified to assist in the reclamation of polluted meat.

There are a number of methods for the decontamination and salvage of food. These are:

1) Aeration and ventilation
2) Cutting away or separating and discarding the polluted portions
3) Heating and cooking
4) Washing
5) Decontamination of containers
6) Other methods, such as vacuum separation, cleaning or spray evaporation.

The method or combination of methods to use depends on the factors mentioned on page 135.

The effect of chemical agents on foods from the point of view of poisoning the food is discussed in Chapter III. In addition, it must be noted that chemical warfare agents may contaminate foods and seriously impair their palatability without rendering them harmful to the consumer.

The following simple rules should act as a guide in the salvaging of foods:

1. Foods seriously contaminated with mustard gas, particularly fatty foods, should be discarded.

2. All arsenical war gases are systemic poisons; therefore, foods contaminated with them should be destroyed.

3. Foods seriously contaminated with non-persistent agents or less toxic agents should also be discarded except in a serious emergency when salvage should be attempted.

4. Foods contaminated only slightly with non-persistent agents or less toxic agents may be salvaged.

5. Foods contaminated with solid white phosphorus are poisonous and must be discarded.

6. Foods which are discarded for use for human beings may possibly be reclaimed for industrial purposes.

7. If one is doubtful about the wholesomeness of any food, discard or destroy it.

1. AERATION AND VENTILATION[2]

Decontamination of most foods can be brought about mainly by airing, after having removed as much as possible of the heavily contaminated parts. All aeration should take place under conditions which permit a slight draft across as much surface as possible of the polluted food or food package. Increase in temperature will hasten evaporation of the chemical agent and thus assist in ventilation but such an increase is not always permissible and will generally be difficult to arrange unless the salvaging place is equipped for heating.

If means are available for producing a violent draft or if forced ventilation can be provided, it may be found to be of help with certain exceptional packages. Often, however, this treatment produces no additional effect since the rate of airing is governed by the rates of desorption and diffusion.

A good type of rack for the aeration of foods can be constructed from expanding metal nets of the type used in road making set on angle iron frames. Old bed frames suitably treated and painted could serve for this purpose.

Unused wading pools and shelters on unused sea beaches provide good situations for the aeration of polluted foods.

When lung irritant and non-persistent tear gases are present, if aeration, ventilation, heating etc. results in dispelling all traces of the odor or other subjective indication, the food may be considered safe and, provided that the palatability has not been seriously impaired, fit for consumption. The presence of slight but dangerous residual traces of mustard gas or of toxic products derived from Lewisite or other arsenical agents can, however, only be ascertained by chemical or biochemical examination or by both.

2. CUTTING AWAY POLLUTED PORTIONS

The proportion of contaminated portions of food to be cut away is almost self-evident. In the case of meat, as mentioned before, an expert butcher should supervise. The general rule to follow is to cut away sufficient depth of the foodstuff to be certain that no gas has penetrated beyond that depth. In most instances an inch or so will suffice, provided, of course, that

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[2] Page, *J. Roy. Sanit. Inst.*, **61**, 155 (1941).

salvage operations have started within a relatively short period after the food became contaminated.

One may be guided as to what depth to cut foods contaminated by phosgene, for instance, by the depth to which the food had been bleached.

The depth to which to cut may also be estimated by the use of chemical analyses.

Where food is in stacks, piles or packages, it may be sufficient to take the outside layers, discard these and ventilate the rest.

It is best to ventilate and air all food that has to be salvaged by cutting away or separating contaminated portions.

3. HEATING AND COOKING

As previously explained, some war gases are readily volatile and others hydrolyze on boiling with water to relatively harmless substances. Hence, some polluted foods can be salvaged by heating and cooking. In particular, foods contaminated by non-persistent agents such as phosgene may be reclaimed by such means. For instance, fresh vegetables and dried fruits may be salvaged by cooking after contamination by phosgene vapor.

This method cannot be used on foods which may be spoiled by heating.

4. WASHING

Reclamation of foods by washing is a limited process, because once the liquid contaminant has penetrated the food, washing has little effect on its removal. However, foods packaged in impervious containers or in water resistant materials may be cleansed by washing. Vegetables which have been polluted only by vapor may at times be salvaged by thorough washing and subsequent aeration. Fish contaminated by war gas vapor may be reclaimed by washing in a solution of chloride of lime.

5. DECONTAMINATION OF CONTAINERS

Foods packed in tin containers will be safe from pollution by poison gas. However, if the can itself is contaminated, a person may become a gas casualty first through contact with the package and second by transferring the contamination to the food when the can is opened. If the canned food has been exposed only to the vapors of chemical agents, washing and aeration will be sufficient. If, however, the cans have been splashed or sprayed, then it is best to decontaminate them by dipping into a cream of bleaching powder or by swabbing with chlorinated lime cream. It should be remembered that the labels become grossly contamined in such instances and should be destroyed. Furthermore, the chlorinated lime cream should not be left in contact with the can too long because of corrosion. The cans should be thoroughly washed after the bleach treatment.

The same observations apply to foods hermetically sealed in glass containers, in metal drums, in metal-lined casks and the like.

Some of these containers can be decontaminated by immersion in boiling water but if the foodstuff may be spoiled by such treatment, this process cannot be used.

6. OTHER METHODS OF DECONTAMINATION AND SALVAGE

In cases where the toxic smokes settle on packaged articles, bags, etc., it should be possible to remove the dust by means of an efficient vacuum cleaner. Then the items could be washed if packed in impervious containers like tins or glass, or aerated.

It may be possible by the use of suction to reclaim foods that are stored in bags in powder form, if the bags become contaminated. Thus, if a bag of flour is immersed in water, the layers next to the bag may become sufficiently wetted to stick to the bag, while the inner contents may be removed by inserting a pipe and applying suction.

A similar mechanism might be set up for the reclamation of other goods packed in bags, like sugar or cereal.

It might be possible also to reclaim certain liquid or powdered foods by making use of a system similar to that used in spray drying. If the food were shot through a nozzle into a heated room, kept partially evacuated, the loss of water and of volatile components would be almost instantaneous.

VI. Protection of Foods[3, 4]

The British Ministry of Food has as the subtitle of its pamphlet "Food and its Protection Against Poison Gas" the following: "The Conservation of Food is Second only to the Preservation of Life." It is well for us to realize the importance of that statement. The United States has an abundance of food but it is necessary for us to conserve this supply not only for emergencies in which we may find ourselves but also to have sufficient food to help our allies.

The best way to obviate the necessity for salvaging foods after gas attacks is to protect them from contamination before the attacks.

The degree of protection of food from liquid gas and, to a lesser extent, from its vapor, is of great importance. This will depend generally on the size of the food stack, on the type of container, if any, and on the system of stacking. Closely stacked piles such as those often found in warehouses are not readily penetrated, even by vapors and what vapor does penetrate the pile is largely absorbed on the outside of the individual packages. Air-

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[3] Ministry of Food, Brit., *Food and its Protection against Poison Gas.* London, 1941.

[4] Page, *J. Roy. Sanit. Inst.*, **61**, 155 (1941).

TABLE 26

PROTECTIVE VALUE OF MATERIALS USED FOR HOLDING OR COVERING FOODS*

NATURE OF COVERING	AGAINST POISON GAS OR VAPOR	AGAINST LIQUID POISON GAS
Sealed metal drums	Complete	Complete
Sealed metal lined cases or casks	Complete	Complete
Hermetically sealed cans, (canned goods)	Complete	Complete
Glass bottles or glazed earthenware fitted with ground stoppers, or with screw caps of metal, bakelite or similar impervious materials	Complete	Complete
Sealed wooden barrels used for the transportation and storage of liquids	Complete	Complete, except in case of heavy and prolonged contamination which impregnates the wood to a significant depth
Transparent cellulose wrappings†	Good	Good
Bags lined with transparent cellulose wrappings	Good	Good
Waxed cartons	Good, if well sealed	Good, if all joints are waxed or covered by a layer of a transparent cellulose wrapping
Metal foil wrappings	Good, if no pinholes	Good, if no pinholes
Cans with lids not hermetically sealed	Fairly good	Good
Glass bottles or glazed vessels with cork stoppers	Fairly good	Good
Bottles and jars covered by greaseproof paper (milk bottles with paper caps)	Fairly good	Moderate, but additional protection can be provided by an outside covering of a transparent cellulose wrapping†
Papier maché cartons	Good, if well sealed	Fairly good. A transparent cellulose wrapping gives additional protection
Oilskins, tarpaulins	Fairly good, but temperature changes are important in intake of vapor	Good

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* Ministry of Food (Brit.) *Food and Its Protection against Poison Gas*, London, 1941.

† Many types of cellulose wrappings are on the market. Those prepared from cellulose, cellulose acetate and nitrocellulose are, in general, good as protective wrappings against gas. Those based on benzyl cellulose are less satisfactory.

TABLE 26—*Continued*

NATURE OF COVERING	AGAINST POISON GAS OR VAPOR	AGAINST LIQUID POISON GAS
Greaseproof papers‡	Good	Fairly good for slight contamination
2- or 3-ply bitumen or tar lined paper	Good	Fairly good for slight contamination
Wooden boxes	Good, if all joints are tight	Poor, soft woods are very absorbent
Thick cardboard boxes	Good, if all joints are tight	Poor, very absorbent
Paper containers	Poor	None
Sacks, canvas, hessian and other textiles	None	None, except when used as screens

‡ Creasing of these papers will greatly diminish their protective value.

ing of such piles is correspondingly difficult and is greatly facilitated by breaking them down. Any airtight or nearly airtight containers, such as sealed cans, metal-lined cases or hermetically-sealed bottles, will give complete protection, although it should be borne in mind that these should be protected from liquid contamination in order to save work for if the outsides are contaminated, labor must be used to decontaminate them. Ordinary soft wood boxes, if well fitted and especially if lined with greaseproof paper, give considerable protection against vapor but very little against liquids, since these readily soak into the wood and appear on the inside surfaces. Thick cardboard is worse than soft wood. Successive wrappings of any material which is not easily penetrable by vapors, such as greaseproof paper, greatly increase the protection afforded against vapors but, if any contamination occurs, they will correspondingly hinder airing. Textiles of any sort are useless by themselves. They are of some assistance in absorbing vapors or in spreading liquid when used as outer coverings, if the inner coverings consist of layers of some impervious paper. They are also of value as screens to prevent liquid from being splashed or sprayed on to piles of goods. Ordinary porous papers can be partially gas-proofed by being covered with paste and thus treated, they may form a useful substitute for the greaseproof or transparent cellulose wrappings now no longer available. Tarpaulins, if in sound condition, afford good protection provided there is sufficient overlap at the joints. If they are covering an otherwise airtight storage space, such as a barge, it is possible that vapor derived from splashes of a slightly volatile liquid may be drawn into the space as expansion and contraction of the air occurs in reponse to changes of temperature and pressure.

The protection of foodstuffs against the solid chemicals which are used in the form of finely dispersed invisible "smokes" is not so difficult. Such particles penetrate all ordinary fabrics and cracks but, just as with similar clouds used in certain systems of spraying and fumigation, most wrappings will be impervious to them. These clouds are easily blown about by drafts. In still air, however, they tend to settle much more on horizontal than on vertical surfaces. Since the solid sneezing "gases" are arsenical compounds, unprotected foods contaminated by these agents may become poisonous. This matter has been discussed in Chapter III, page 51.

In Table 26 the protective ratings against chemical agents of the more commonly used containers and coverings are tabulated. It is to be noted that metal containers splashed with some of the more acid or corrosive agents like the chlorosulfonic acids may be seriously corroded and food spoilage may result.

Protective Measures for Large Quantities of Foods Stored in Warehouses

The protective measures to be used for safeguarding bulk stores of food in warehouses, docks, and other places where such large stores are held may be summarized as follows.

1. Foods in containers or wrappings which afford little or no protection against chemical agents should not be stored on the top floors or in the basements of such buildings.

2. Waterproofed canvas covers, water repellant duck covers, impervious tarpaulins, rubber sheeting, if available, and oilskins are probably the best means for covering stocks of foodstuffs in packages. They give good protection against oily splashes of chemical agents.

3. These impervious sheetings should cover the piles of packages as closely as possible but, when this is inconvenient, they should be hung as screens by means of hooks or frames. Where free circulation of air is necessary for proper storage, as in the case of fresh fruit in crates, these covers should be arranged so that they can be readily pulled into position as soon as an air raid warning is given.

4. When waterproof canvas or other impervious coverings are not available, ordinary canvas or sacking can be used to provide covering. These covers provide little protection against the vapor of chemical agents but they do reduce the contamination resulting from splashes of war gas.

5. Foods stored in freezers or refrigerated rooms need no additional protection, provided the doors are reasonably air tight and precautions have been taken against blowing or drawing the chemical agent into the freezer by means of the ventilating system.

6. Food should be stored in close stacks and should not be permitted to lie scattered about the warehouse floors. Such stacking affords good protection for the packages on the interior of the pile.

Similar precautions should be observed on a smaller scale, of course, by retail food stores, institutions and hotels where relatively large stores of food are held.

To protect food at home, place as many as possible of the bottles, jars, canned goods, or other sealed containers inside closets with wooden doors or in strong wooden boxes with well-fitting covers. Store most of your food in tin cans with close fitting covers or in bottles with plastic screw caps. This is especially important for foods such as sugar, flour, or cereals, which are generally bought in easily penetrable coverings. The domestic refrigerator or ice box is sufficiently air tight to provide a gas proof storage place.

APPENDIX

TABLE I

CONVERSION TABLE FOR GASES AND VAPORS[1]

(milligrams per liter to parts per million and vice versa)

[25° C. and 760 mm. mercury, barometric pressure.]

MOLECULAR WEIGHT	1 MG./L. PPM.	1 PPM. MG./L.	MOLECULAR WEIGHT	1 MG./L. PPM.	1 PPM. MG./L.	MOLECULAR WEIGHT	1 MG./L. PPM.	1 PPM. MG./L.
1	24,450	0.0000409	34	719	0.001391	67	365	0.00274
2	12,230	.0000818	35	699	.001432	68	360	.00278
3	8,150	.0001227	36	679	.001472	69	354	.00282
4	6,113	.0001636	37	661	.001513	70	349	.00286
5	4,890	.0002045	38	643	.001554	71	344	.00290
6	4,075	.0002454	39	627	.001595	72	340	.00294
7	3,493	.0002863	40	611	.001636	73	335	.00299
8	3,056	.000327	41	596	.001677	74	330	.00303
9	2,717	.000368	42	582	.001718	75	326	.00307
10	2,445	.000409	43	569	.001759	76	322	.00311
11	2,223	.000450	44	556	.001800	77	318	.00315
12	2,038	.000491	45	543	.001840	78	313	.00319
13	1,881	.000532	46	532	.001881	79	309	.00323
14	1,746	.000573	47	520	.001922	80	306	.00327
15	1,630	.000614	48	509	.001963	81	302	.00331
16	1,528	.000654	49	499	.002004	82	298	.00335
17	1,438	.000695	50	489	.002045	83	295	.00339
18	1,358	.000736	51	479	.002086	84	291	.00344
19	1,287	.000777	52	470	.002127	85	288	.00348
20	1,223	.000818	53	461	.002168	86	284	.00352
21	1,164	.000859	54	453	.002209	87	281	.00356
22	1,111	.000900	55	445	.002250	88	278	.00360
23	1,063	.000941	56	437	.002290	89	275	.00364
24	1,019	.000982	57	429	.002331	90	272	.00368
25	978	.001022	58	422	.002372	91	269	.00372
26	940	.001063	59	414	.002413	92	266	.00376
27	906	.001104	60	408	.002554	93	263	.00380
28	873	.001145	61	401	.002495	94	260	.00384
29	843	.001186	62	394	.00254	95	257	.00389
30	815	.001227	63	388	.00258	96	255	.00393
31	789	.001268	64	382	.00262	97	252	.00397
32	764	.001309	65	376	.00266	98	249.5	.00401
33	741	.001350	66	370	.00270	99	247.0	.00405

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[1] Fieldner, Katz and Kinney, "Gas Masks for Gases Met in Fighting Fires." *U. S. Bur. Mines, Tech. Papers* **248** (1921).

TABLE I—*Continued*

MOLECULAR WEIGHT	1 MG./L. PPM.	1 PPM. MG./L.	MOLECULAR WEIGHT	1 MG./L. PPM.	1 PPM. MG./L.	MOLECULAR WEIGHT	1 MG./L. PPM.	1 PPM. MG./L.
100	244.5	0.00409	145	168.6	0.00593	190	128.7	0.00777
101	242.1	.00413	146	167.5	.00597	191	128.0	.00781
102	239.7	.00417	147	166.3	.00601	192	127.3	.00785
103	237.4	.00421	148	165.2	.00605	193	126.7	.00789
104	235.1	.00425	149	164.1	.00609	194	126.0	.00793
105	232.9	.00429	150	163.0	.00613	195	125.4	.00798
106	230.7	.00434	151	161.9	.00618	196	124.7	.00802
107	228.5	.00438	152	160.9	.00622	197	124.1	.00806
108	226.4	.00442	153	159.8	.00626	198	123.5	.00810
109	224.3	.00446	154	158.8	.00630	199	122.9	.00814
110	222.3	.00450	155	157.7	.00634	200	122.3	.00818
111	220.3	.00454	156	156.7	.00638	201	121.6	.00822
112	218.3	.00458	157	155.7	.00642	202	121.0	.00826
113	216.4	.00462	158	154.7	.00646	203	120.4	.00830
114	214.5	.00466	159	153.7	.00650	204	119.9	.00834
115	212.6	.00470	160	152.8	.00654	205	119.3	.00838
116	210.8	.00474	161	151.9	.00658	206	118.7	.00843
117	209.0	.00479	162	150.9	.00663	207	118.1	.00847
118	207.2	.00483	163	150.0	.00667	208	117.5	.00851
119	205.5	.00487	164	149.1	.00671	209	117.0	.00855
120	203.8	.00491	165	148.2	.00675	210	116.4	.00859
121	202.1	.00495	166	147.3	.00679	211	115.9	.00863
122	200.4	.00499	167	146.4	.00683	212	115.3	.00867
123	198.8	.00503	168	145.5	.00687	213	114.8	.00871
124	197.2	.00507	169	144.7	.00691	214	114.3	.00875
125	195.6	.00511	170	143.8	.00695	215	113.7	.00879
126	194.0	.00515	171	143.0	.00699	216	113.2	.00883
127	192.5	.00519	172	142.2	.00703	217	112.7	.00888
128	191.0	.00524	173	141.3	.00708	218	112.2	.00892
129	189.5	.00528	174	140.5	.00712	219	111.6	.00896
130	188.1	.00532	175	139.7	.00716	220	111.1	.00900
131	186.6	.00536	176	138.9	.00720	221	110.6	.00904
132	185.2	.00540	177	138.1	.00724	222	110.1	.00908
133	183.8	.00544	178	137.4	.00728	223	109.6	.00912
134	182.5	.00548	179	136.6	.00732	224	109.2	.00916
135	181.1	.00552	180	135.8	.00736	225	108.7	.00920
136	179.8	.00556	181	135.1	.00740	226	108.2	.00924
137	178.5	.00560	182	134.3	.00744	227	107.7	.00928
138	177.2	.00564	183	133.6	.00748	228	107.2	.00933
139	175.9	.00569	184	132.9	.00753	229	106.8	.00937
140	174.6	.00573	185	132.2	.00757	230	106.3	.00941
141	173.4	.00577	186	131.5	.00761	231	105.8	.00945
142	172.2	.00581	187	130.7	.00765	232	105.4	.00949
143	171.0	.00585	188	130.1	.00769	233	104.9	.00953
144	169.8	.00589	189	129.4	.00773	234	104.5	.00957

TABLE I—*Concluded*

MOLECULAR WEIGHT	1 MG./L. PPM.	1 PPM. MG./L.	MOLECULAR WEIGHT	1 MG./L. PPM.	1 PPM. MG./L.	MOLECULAR WEIGHT	1 MG./L. PPM.	1 PPM. MG./L.
235	104.0	0.00961	257	95.1	0.01051	279	87.6	0.01141
236	103.6	.00965	258	94.8	.01055	280	87.3	.01145
237	103.2	.00969	259	94.4	.01059	281	87.0	.01149
238	102.7	.00973	260	94.0	.01063	282	86.7	.01153
239	102.3	.00978	261	93.7	.01067	283	86.4	.01157
240	101.9	.00982	262	93.3	.01072	284	86.1	.01162
241	101.5	.00986	263	93.0	.01076	285	85.8	.01166
242	101.0	.00990	264	92.6	.01080	286	85.5	.01170
243	100.6	.00994	265	92.3	.01084	287	85.2	.01174
244	100.2	.00998	266	91.9	.01088	288	84.9	.01178
245	99.8	.01002	267	91.6	.01092	289	84.6	.01182
246	99.4	.01006	268	91.2	.01096	290	84.3	.01186
247	99.0	.01010	269	90.9	.01100	291	84.0	.01190
248	98.6	.01014	270	90.6	.01104	292	83.7	.01194
249	98.2	.01018	271	90.2	.01108	293	83.4	.01198
250	97.8	.01022	272	89.9	.01112	294	83.2	.01202
251	97.4	.01027	273	89.6	.01117	295	82.9	.01207
252	97.0	.01031	274	89.2	.01121	296	82.6	.01211
253	96.6	.01035	275	88.9	.01125	297	82.3	.01215
254	96.3	.01039	276	88.6	.01129	298	82.0	.01219
255	95.9	.01043	277	88.3	.01133	299	81.8	.01223
256	95.5	.01047	278	87.9	.01137	300	81.5	.01227

Table II
The Physical Constants of the Chemical Warfare Agents

	Molecular weight	M. P., ° C.	B. P., ° C. @760 mm.	Density D_4^{20}	Vapor density, S.T.P., air = 1	Vapor pressure, 20° C., mm. Hg.	Saturation concn., volatility, mg./l., 20° C.	Persistence at 20 ° C. (approx. rel. time for evap.) H_2O = 1
Lung Irritants								
Chlorine	70.9	−102	−33.6	(1.4)	2.4	5,031	∞	Non-persistent
Bromine	159.8	−7	59	3.1	5.5	172	∞	Non-persistent
Phosgene	98.9	−104	8.3	1.38	3.5	1,180	∞	Non-persistent
Diphosgene	197.9	−57	128	1.65	6.9	10.3	112	0.38
Chloromethylchloroformate	129		107	1.47	4.5	5.6		
Chloropicrin	164.5	−69	112	1.66	5.7	18.3	165	0.23
Phenylcarbylamine chloride	175		208	1.3	6.0		2.1	
Dimethyl sulfate	126	−31.7	188	1.33	4.3		3.3	
Methylchlorosulfonate	130.5	−70	133	1.49	4.5		60	
Ethylchlorosulfonate	144.5		152	1.4	5		18	
Irritants								
Lachrymators								
Ethylbromoacetate	167		168	1.53	5.8		21	
Ethyliodoacetate	214	−21	179	1.8	7.4	0.54	6.3	6.9
Methylchloroformate	94.5		71.4	1.23	3.9			
Bromoacetone	137	−54	136	1.63	4.7	9	68	0.5
Bromomethylethyl ketone	151		145	1.43	5.2		34	
Chloroacetophenone	154.5	58	247	1.32	5.3	0.013	0.10	Non-persistent cloud
Benzyl bromide	171	−4	199	1.43	5.8		0.244	
Xylyl bromide	185		210–20	1.4	6.4	0.07	0.7	58
Bromobenzyl cyanide	196	25.4	242(d.)	1.52	6.8	0.012	0.13	325
Sulfuryl chloride	135	−54.1	69.1	1.67	4.6			

Toxic Smokes								
Diphenylchloroarsine	264.5	44	383	1.4		0.0005		Non-persistent cloud
Diphenylaminechloroarsine	277.5	195	410	1.65		2×10^{-13}		Non-persistent cloud
Diphenylcyanoarsine	255	33	377	1.45		0.0002		Non-persistent cloud
Labyrinthic gases								
Dichloromethyl ether	114.7		105	1.3	4	180		
Dibromomethyl ether	204	−34	154	2.2	7	21		
Vesicants								
Dichloroethyl sulfide	159	14.4	217(d.)	1.27	5.4	0.11	0.96	38
Lewisite	207.3	−18.2	190(d.)	1.89	7.1	0.4	4.5	9.5
Methyldichloroarsine	161	42.5	133	1.84	5.5	8.5	75	0.5
Ethyldichloroarsine	175	−30	155	1.66	6.0	23	22–50	1.8
Phenyldichloroarsine	223	−20	257	1.6	7.7	0.4		
Systemic poisons								
Hydrogen cyanide	27	−15	26.5	0.7	0.94	610	901	0.02
Cyanogen chloride	61.4	−6	12.5	1.2	2.1	1,001	3,300	
Cyanogen bromide	106	52	61	1.9	3.7	89	200	
Carbon monoxide	28	−207	−192		0.97			
Hydrogen sulfide	34.1	−82.9	−61.8		1.19		16,500[1]	
Screening smokes								
Titanium tetrachloride	189.7	−30	136.4	1.73				
FS		<−30	80	1.9				
White phosphorus (P_4)	124.1	44[2]	280	1.82				

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[1] At 10° C.

[2] Ignites at 34° C.

Table III

Order of Toxicity of the War Gases[1, 2]

(Toxicity of Chlorine = 1.0)

SUBSTANCE		SUBSTANCE	
Sulfuryl chloride	0.16	Ethylchloroformate	2.6
Chromyl chloride	0.3	Methylchlorosulfonate (pure)	2.5
Bromine	0.5	Methyl formate	2.6
Methylchlorosulfonate	0.8	Methylchloroformate	3.0
Monochloroethylchloroformate	0.8	Proprionyl bromide	3.3
Trichloroethylmercaptan	1.0	Dichloroethyl sulfide (mustard gas)	8.8
Chlorine	1.0	Cyanogen chloride	13.5
Ethyliodoacetate	1.3	Diphosgene, technically pure	16.0
Bromobutyrl bromide	1.4	Hydrocyanic acid	16.5
Arsenic trichloride	1.5	Diphosgene, chemically pure	27.0
Trichloroethylchloroformate	1.6	Yperite (mustard) (American. data)	15–30
Chloropicrin	2.2		

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[1] Chlopin, Z. *ges. Schiess-u. Sprengstoffwesen*, **22, 23** (1927–28).

[2] Flury and Zernik, *Schaedliche Gase*. Springer, Berlin, 1931.

Table IV

Most Important War Gases of World War 1914–1918

Acrolein
Arsenic trichloride
Benzyl bromide
Benzyl iodide
Bromoacetone
Bromobenzyl cyanide
Bromoacetic acid esters
Butylmercaptan
Chloropicrin
Cyanogen bromide
Chlorine
Chloroacetone
Chloroacetophenone
Chlorovinyldichloroarsine (Lewisite)
Dibromomethyl ether
Dichloroethyl sulfide
Dichloromethyl ether
Dimethyl sulfate
Diphenylaminechloroarsine
Diphenylchloroarsine
Diphenylcyanoarsine
Diphosgene
Ethyliodoacetate
Ethyldichloroarsine
Hydrogen cyanide
Methylchlorocarbonate (Methylchloroformate)
Methyl and ethylchlorosulfonates
Perchloromethylmercaptan
Phenylcarbylamine chloride
Phosgene
Sulfur monochloride
Thiophosgene
Xylyl bromide

Table V

Military Symbols and Names for War Gases[1]

SYMBOL	COUNTRY	CHEMICAL NAME
Adamsite	English	Diphenylaminechloroarsine
Aquinite	French	Chloropicrin
A-Stoff	German	Chloroacetone
BA	British	Bromoacetone
BBC	British	Bromobenzyl cyanide
Be-grenades	Austrian	Bromoacetone
Berger mixture	British	Zinc, zinc oxide, carbon tetrachloride and kieselguhr (screening smoke)
Berthollite	French	Chlorine
Bibi	French	Dibromomethyl ether
Blue cross	German	Diphenylchloroarsine and diphenylcyanoarsine
BM	British	Zinc, carbon tetrachloride, sodium chlorate, ammonium chloride and magnesium carbonate (screening smoke)
Bn-Stoff	German	Bromomethylethyl ketone
Bromlost	German	Dibromoethyl sulfide
B-Stoff	German	Bromoacetone and brominated ketones
CA	American	Bromobenzyl cyanide
CAP	British	Chloroacetophenone
Camite	French	Bromobenzyl cyanide
Campiellite	Italian	Cyanogen bromide and bromoacetone
CD	British	Diphenylcyanoarsine
CDA	American	Diphenylcyanoarsine
Ce-grenades	Austrian	Cyanogen bromide
CG	American	Phosgene
Cici	French	Dichloromethyl ether
Cl	American	Chlorine
Clairsite	French	Perchloromethylmercaptan
Clark I	German	Diphenylchloroarsine
Clark II	German	Diphenylcyanoarsine
Collongite	French	Phosgene
CN	American	Chloroacetophenone
CNB	American	Chloroacetophenone, benzene, carbon tetrachloride
CNS	American	Chloroacetophenone, chloropicrin and chloroform
C-Stoff	German	Methylchloroformate
Cyclite	French	Benzyl bromide
DA	American	Diphenylchloroarsine
Dick D	German	Ethyldichloroarsine
Diphosgene	English	Trichloromethylchloroformate
DM	American	Diphenylaminechloroarsine
D-Stoff	German	Dimethyl sulfate, also phosgene
ED	American	Ethyldichlorarsine

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[1] Flury and Zernik, *Schaedliche Gases.* Springer, Berlin, 1931.

TABLE V—*Concluded*

SYMBOL	COUNTRY	CHEMICAL NAME
E-Stoff	German	Cyanogen bromide
Forestite	French	Hydrocyanic acid
FM	American	Titanium tetrachloride
Fraisinite	French	Benzyl iodide
F-Stoff	German	Titanium tetrachloride
Green cross	German	Chloropicrin and diphosgene also in part ethyldichloroarsine, ethyldibromoarsine, dichloromethyl ether, and bromomethylethyl ketone
HC	American	Zinc, zinc oxide and hexachloroethane (screening smoke)
Homomartonite	French	Bromomethylethyl ketone
HS	American	Dichloroethyl sulfide
Klopp	German	Chloropicrin
KSK	British	Ethyliodoacetate
K-Stoff	German	Methylchloroformate
Lacrimite	French	Thiophosgene
Lewisite	American	Chlorovinyldichloroarsine
Lost	German	Dichloroethyl sulfide
M1	American	Chlorovinyldichloroarsine
Manganite	French	Hydrogen cyanide and arsenic trichloride
Marsite	French	Arsenic trichloride
Martonite	French	Bromoacetone and brominated ketones
Mauguinite	French	Cyanogen chloride
Methyldick	German	Methyldichloroarsine
Mustard gas	English	Dichloroethyl sulfide
NC mixture	German	Chloropicrin and zinc tetrachloride
Ni-Stoff	German	Dianisidin
Opacite	French	Zinc tetrachloride
Palite	French	Monochloromethylchloroformate
Papite	French	Acrolein
Per-Stoff	German	Diphosgene
PS	American	Chloropicrin
Rationite	French	Dimethyl sulfate
Senfgas	German	Dichloroethyl sulfide
Sternite	French	Diphenylchloroarsine and diphenylcyanoarsine
Sulvinite	French	Ethylchlorosulfonate
Superpalite	French	Diphosgene
Surpalite	French	Diphosgene
Tonite	French	Chloroacetone
T-Stoff	German	Xylyl bromide
Villantite	French	Methylchlorosulfonate
Vincennite	French	Arsenic trichloride and hydrogen cyanide
Vitrite	French	Cyanogen chloride and arsenic trichloride
Vomiting Gas	English	Chloropicrin
WP	American	White phosphorus
Yellow cross	German	Dichloroethyl sulfide, also in part, ethyldichloroarsine, dichloromethyl ether
Yperite	French	Dichloroethyl sulfide

AUTHOR INDEX

SUBJECT INDEX

Zelda J. Lurie